GAS CHROMATOGRAPHY

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Second International Symposium Held Under the Auspices of the Analysis Instrumentation Division of the Instrument Society of America, June, 1959

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FOREWORD

The Instrument Society of America's Second International Symposium on Gas Chromatography was held at the Kellogg Center for Continuing Education, Michigan State University, June 10 through 13, 1959. The following collection of papers represents the proceedings of this meeting.

This meeting followed the pattern that was found to be successful at the first symposium, held at the same location in 1957. Papers were scheduled for presentation in morning and evening sessions, with the afternoons left open for recreation or free discussion of the papers or topics selected by the participants. In this manner, everyone had an opportunity to present detailed views in an uninhibited manner "from his own soap box." This method, we believe, provides maximum opportunity for the interchange of information and stimulation of ideas for future experimentation

We believe the basic reason for the existence of technical societies or meeting groups is the stimulation of ideas through mutual contact, careful documentation in the form of technical papers, and selective dissemination of these papers and other pertinent technical information. The effectiveness of a technical society lies not only in the competence and initiative of its members, but also in the technical support of the advanced investigators in their respective fields. We are in high hopes that the ISA organization, and particularly the facilities of the Analysis Instrumentation Division, will continue to be recognized and utilized by all technical people interested in instrumentation.

We wish to express our thanks to the contributors, session chairmen, and many other people who have contributed to this effort. The assistance of Mr. Thomas Collins, Dr. Tunis Dekker, and their staffs, of the Kellogg Center, is deeply appreciated. We wish to express a great measure of our thanks to Jean McDonald for her competent assistance to the General Chairman in handling the numerous details, correspondence, and arrangements necessary for the success of this meeting.

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CONTENTS

CHAPTER I

Effect of Flow Rate on Optimum Sample Size for Minimum Values of Retention Time and HETP

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While investigating several compounds as possible substrates for the analysis of esters and alcohols, the researchers in the Chemical Engineering Department at Iowa State College noticed (*1*) that at constant operating conditions, retention time and the height equivalent to a theoretical plate (HETP) are affected by the size of the sample used for analysis. At the carrier gas flow rate of 5.0 ml helium per minute, definite minima were obtained in the curves for retention time and HETP as functions of sample size. These minima were observed for a six-component alcohol test mixture and a four-component ester test mixture in dibutyl sebacate and dibutyl phthalate columns of 4.6 mm internal diameter by approximately 130 cm long.

The presence of these minima was thought to be caused by diffusion effects at the low flow rate used; consequently, a similar study was made to determine the effect of varying the flow rate on the optimum sample size for minimum values of retention time and HETP. Specifically, the experimental work reported here was designed to show whether or not the minima were present at all flow rates; and if they were present, to determine the effect of flow rate on their location. Because of the work involved, this study was limited to the ester test mixture previously investigated: ethyl formate, vinyl acetate, ethyl acetate, and isopropyl acetate. The same dibutyl sebacate column was used as in the earlier research.

EXPERIMENTAL

Apparatus

The system used for analysis is shown graphically in Fig. 1. Details of the column and accessories are shown in Fig. 2. The column consisted of a length of 4.6-mm ID borosilicate glass tubing surrounded by a vapor jacket made from a 135-cm long section of 5.1-cm ID glass tubing. Packed length was 130.4 cm. The column assembly was in the form of a condenser and had a stopcock at the bottom to allow removal of condensate. The column exit was connected to the thermal conductivity cell through a ball joint with 1.5-mm bore capillary glass tubing. The sample injection tee

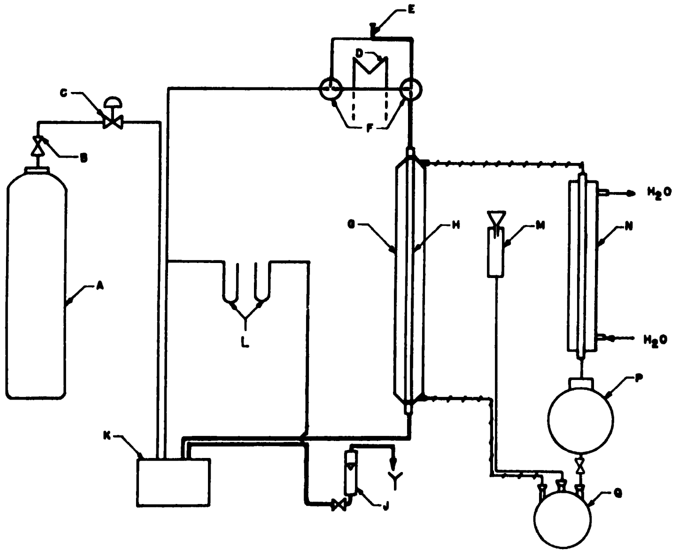

FIG 1 Flow diagram for partition chromatographic analysis A: helium cylinder, B helium valve, C two-stage cylinder regulator, D sample heater, E sample injection tee; F three-way stopcock; G vapor jacket, H partition column; J rotameter, K thermal conductivity cell; L. manometer, M make-up flask, N vapor condenser; P· reflux accumulator; Q· solvent boiler

KEY. Thin line—helium; heavy line—helium and sample, hatched line—vapor

was kept at approximately 170°C by the cone of a small radiant heater of the common household variety. This ensured rapid and complete vaporization of the sample.

A Model TR-II-B Gow-Mac thermal conductivity cell, geometry 9193, was used with a Model 9293-B Gow-Mac power supply control unit. The bridge current was maintained at 175 ma. The thermal conductivity cell was kept at 200°C with an integral heater and thermoswitch. Data were recorded with a Bristol Model IPH-570 adjustable range-adjustable zero Dynamaster potentiometer, with the range set at 0–10 mv. Chart speed was 30 in. per hour. The helium flow rates were maintained constant by a Brooks "Sho Rate" 150 rotameter with an integrally mounted constant differential pressure relay. The use of a two-stage cylinder regulator, with the additional stage at the rotameter, resulted in constant carrier gas flow rates as the cylinder emptied.

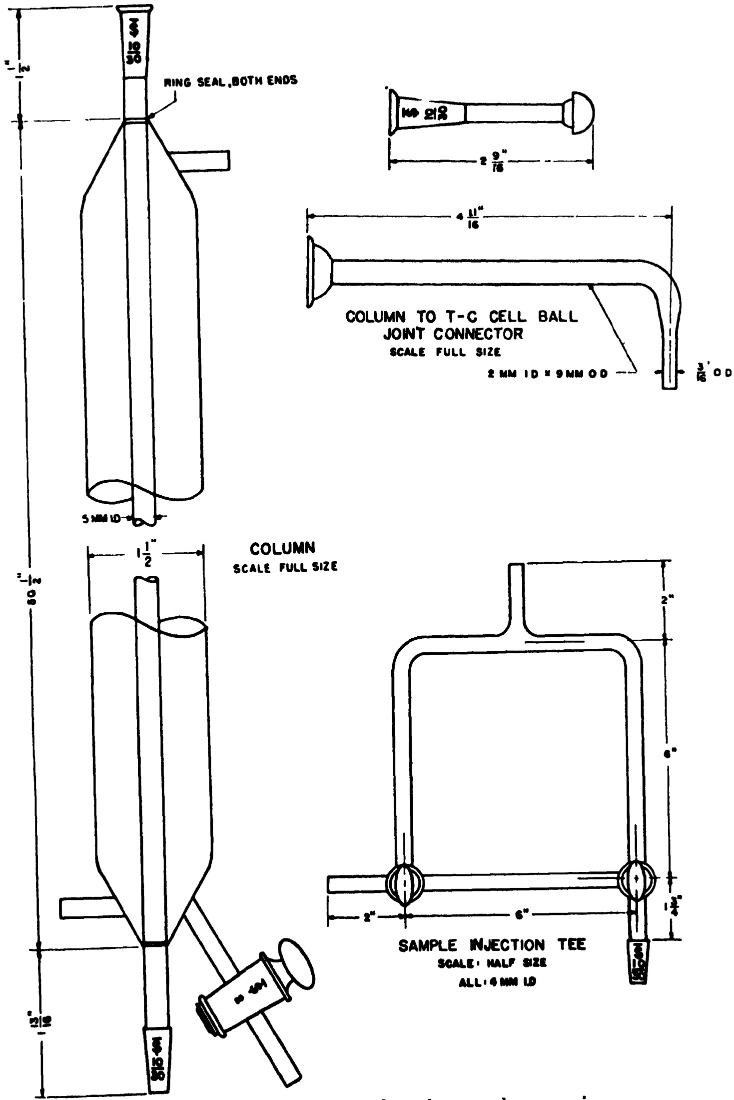

FIG 2. Details of chromatography column and accessories.

Procedure

The packing, 35 parts by weight of dibutyl sebacate per 100 parts by weight of −48+65 mesh Johns-Manville type C-22 firebrick, was prepared by the method of Evans and Willard (*3*). Uniformity of packing was ensured by the use of an electric vibrator for filling the column A porous plug of glass wool was inserted at both ends of the packed section to prevent any solid material from being carried into the detector or the loss of any packing if the sample injection assembly were blown off by a sudden change in supply pressure. Refluxing methanol at 64 8°C. in the column vapor jacket provided a constant operating temperature. For these tests, the column inlet and outlet pressures were 613 5 and 13.5 mm mercury above atmospheric, respectively, regardless of changes in flow rate

The apparatus was allowed to come to thermal equilibrium as indicated on the recorder chart by a straight horizontal line for 10 minutes Successively larger samples of the test mixture were then injected through a rubber serum cap into the column with a microsyringe. This procedure was repeated for the following flow rates 27.5, 50 6, 61 8, and 76 5 ml helium per minute, measured at room temperature and column outlet pressure. Injection time was less than 2 seconds in all cases.

The determination of sample size was as follows. Having determined the density of the test mixture with a pycnometer, several sizes of hypodermic needles were calibrated by weighing 10 drops into a tared serum bottle through a self-sealing rubber stopper. This was repeated three times for each needle The deviation in weight for a 10-drop sample was less than 0 3% for all needles. The volume of an average drop from each needle was then calculated. The needle calibrations have been previously given (*1*).

RESULTS

As was expected from the data presented by numerous other workers, the primary effect of increasing the flow rate at a constant sample size is to decrease materially the retention times of the sample components This can be seen in Figs 3–6 in the 1- to 2-minute decrease in retention time for any solute at constant sample size as the flow rate increases. It is interesting to note that the effect of flow rate on retention time becomes more pronounced as the sample size is increased.

The result of independently varying sample size and flow rate, shown in Figs. 3–6, indicates that each flow rate in the range tested has a corresponding optimum sample size for obtaining the shortest possible retention times. The curves for 5.0 ml helium per minute have been reproduced here from previous work (*1*) for purposes of comparison. The effect of increasing the flow rate is to increase the optimum sample size. This is seen in the move-

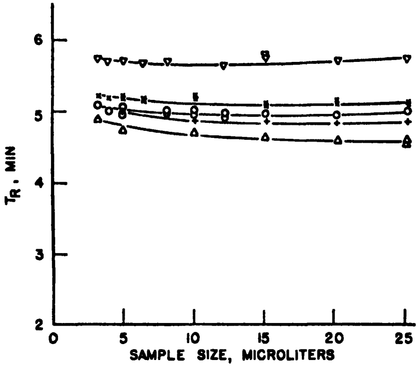

FIG. 3 Effect of flow rate on minimum retention time for ethyl formate
KEY Milliliters of helium per minute—∇, 5.0; ×, 27.5; ○, 50.6, +, 61.8, △, 76.5

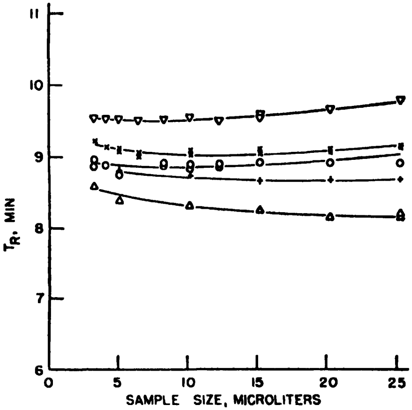

FIG. 4 Effect of flow rate on minimum retention time for vinyl acetate
KEY Milliliters of helium per minute—∇, 5.0; ×, 27.5; ○, 50.6, +, 61.8; △, 76.5.

ment to the right, in Figs. 3–6, of the curve minima for each test component as the flow rate increases.

In the light of these data, and since similar minima have been obtained with other systems (*1*) previously tested at 5.0 ml per minute, it is thought that the presence of the minima in the retention time-sample size relationship may be regarded as a general phenomenon, at least for oxygenated aliphatics, over the range of carrier gas flow rates usually employed in gas-liquid partition chromatography (GLPC) analysis.

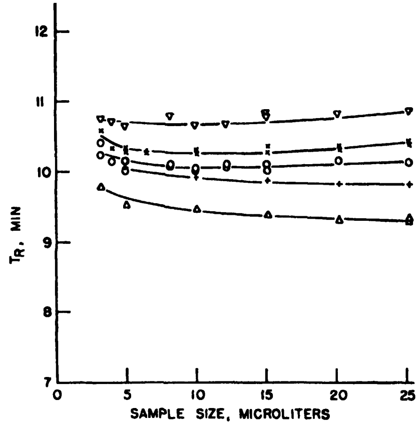

FIG 5 Effect of flow rate on minimum retention time for ethyl acetate
KEY: Milliliters of helium per minute—∇, 5.0, ×, 27.5, ○, 50.6; +, 61.8, △, 76.5

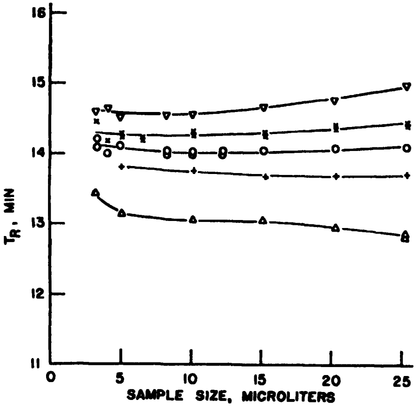

FIG 6 Effect of flow rate on minimum retention time for isopropyl acetate
KEY Milliliters of helium per minute—∇, 5.0; ×, 27.5; ○, 50.6, +, 61.8; △, 76.5.

Upon studying the effect of varying the sample size on the HETP calculated in accordance with the method in Desty (*2*) at a constant flow rate, minimum values of HETP were obtained in previous work done in this laboratory. It is thought that the presence of these minima in the HETP-sample size curves is due to tailing and slow diffusion rates at the low (5.0 ml per minute) helium rate used. The data obtained at that flow rate are

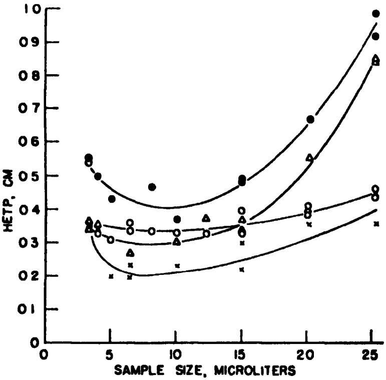

FIG. 7. Effect of sample size on HETP for esters; helium rate, 5.0 ml/min
KEY: ○, Ethyl formate; △, vinyl acetate; ●, ethyl acetate; ×, isopropyl acetate.

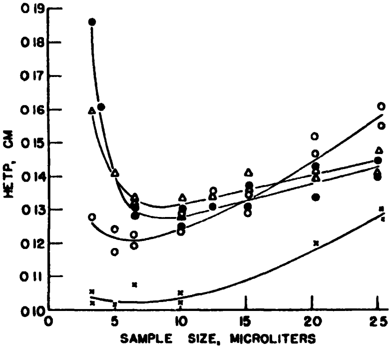

FIG. 8. Effect of sample size on HETP for esters; helium rate 27.5 ml/min
KEY: ○, Ethyl formate; △, vinyl acetate; ●, ethyl acetate; ×, isopropyl acetate

reproduced as Fig. 7. Optimum sample size at this flow rate is 6–10 μl. As can be seen in Fig. 8, the four esters exhibit minimum values of HETP at approximately this same range of sample sizes for a carrier rate of 27.5 ml per minute. Upon increasing the carrier gas rate to 50.6 ml per minute, the optimum sample size drops to 5 μl (Fig. 9). The reason for the flattening out of the curves at samples above 15 μl in size is not known. It is apparent (Fig. 10) that similar minima are present at a carrier flow rate of 76.5 ml per minute. However, the optimum sample increases to 8–12 μl in size. This correlation for the runs at 61.8 ml per minute has not been presented because of apparent scattering of data if the vertical scale is expanded sufficiently to show separate data points.

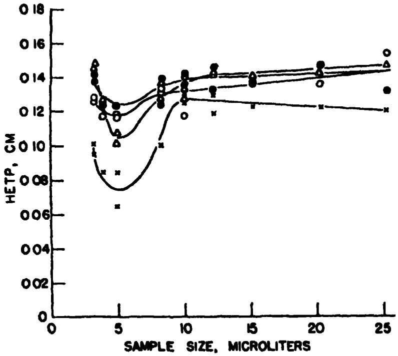

FIG 9 Effect of sample size on HETP for esters, helium rate 50 6 ml/min
KEY: O, Ethyl formate; △, vinyl acetate, ●, ethyl acetate, ×, isopropyl acetate

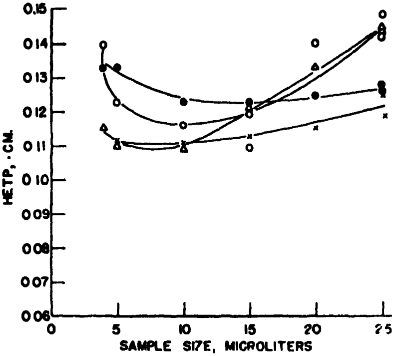

FIG 10 Effect of sample size on HETP for esters, helium rate 76 5 ml/min
KEY: O, Ethyl formate; △, vinyl acetate; ●, ethyl acetate; ×, isopropyl acetate.

It will be noted, by comparing the curves for each sample component in Figs. 7–10, that the column efficiency as measured by the HETP is approximately tripled by raising the flow rate from 5.0 to 27.5 ml per minute. Increasing the flow rate beyond the latter point gives only meager increases in efficiency. For purposes of illustrating this more clearly, a comparison is given in Fig. 11 of the effect of flow rate on HETP with increasing sample size. Ethyl formate is used as being representative of the data obtained. Individual data points are not shown as they appear in Figs. 7–10. The trends shown here are typical of those shown by the other three sample components. This is in agreement with the observations of James and

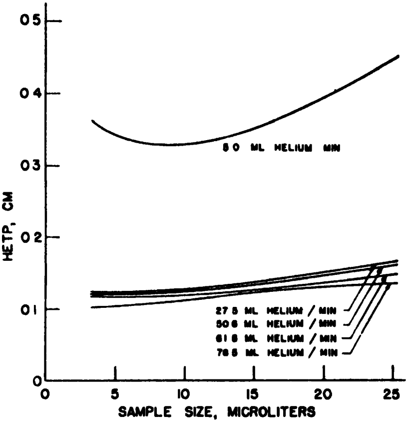

Fig 11 Effect of flow rate on HETP for ethyl formate.

Martin (*4*) and Mellor (*5*), who found that column efficiency is no longer increased by decreasing the flow rate to values below 18 and 25 ml per minute, respectively, for packings of the size used in this work. It must be pointed out that at very high flow rates, the minima in the HETP-sample size curves are not apparent unless the ordinates of the curves are greatly expanded. At high flow rates, the curves of HETP vs. sample size are flatter, probably because of the effect of faster diffusion in the vapor phase. However, as there are pronounced minima at all flow rates, it is believed that curves of this type will in general exhibit minima. The exaggerated appearance of the minima at a carrier rate of 5.0 ml per minute is believed due to the combined effects of low flow rate and diffusion rate.

It is concluded that the retention times show definite optimum sample sizes over the range of 5.0 to 76.5 ml carrier gas per minute; that, as the carrier rate increases, the optimum sample size for minimum value of retention time increases; that the HETP minima previously observed are not due solely to the low flow rate used, but are a general phenomenon; and that it is not feasible to use a carrier rate below approximately 25 ml per minute for separations of this type, due to the great increase in HETP at lower flow rates.

It is thought that advantage may be taken of the presence of the more pronounced minima in the retention time-sample size relationship at lower flow rates to select the sample size which will give the best separation of such closely similar compounds as *cis*- and *trans*-isomers and ortho, meta, and para isomers.

ACKNOWLEDGMENT

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CHAPTER II

Theoretical Considerations in Large Gas Chromatographic Columns

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INTRODUCTION

It is generally accepted that the height equivalent to a theoretical plate (HETP) of gas chromatographic columns increases with their diameter, but so far reports have differed widely as to the magnitude of this increase. Thus, Carle and Johns (*1*) have reported a twentyfold HETP increase when passing from 0.19-inch columns to 3-inch columns, while Evans and his associates (*2*) have reported no apparent HETP increase for up to 3-inch columns.

It seems almost tautological that any increase in HETP with column size is due to some systematic variation across the column diameter, as otherwise a large column could be considered as made up of a more or less large number of small columns, these small columns being characterized by a variance in their individual characteristics which is substantially independent of their number.

Two kinds of systematic variations will be considered in this study. The first will concern the small space near the column walls where the gas flow is larger than in the rest of the column. The second variation will be an assumed variation within the packing from one side of the column to the other.

BOUNDARY LAYER EFFECT

There is near the smooth wall of a packed column a thin boundary layer, of average thickness $\frac{1}{2}h_0$, where h_0 designates the average particle diameter, in which the average passages will be greater than in the rest of the column, where the packing grains intermesh. This boundary layer will be traversed by a carrier gas flow with a velocity $v + v_1$, appreciably greater than the velocity v in the rest of the column. We shall assume that there is an intrinsic HETP, h, of the column interior, which is characteristic of the particular component considered, and which is related to the velocity v and to a minimum HETP, $h_{\min}$, by the relation:

$$h = \frac{2D}{v} + \frac{h_{\min}^2 v}{8D} \qquad (1)$$

where D designates the diffusion coefficient of the molecules of that component.

The value of v for which $h = h_{\min}$ is

$$v_{\text{opt}} = \frac{4D}{h_{\min}} \tag{2}$$

We shall write

$$v_1 = av \tag{3}$$

with the understanding that the factor a lies somewhere between 3 and 6, corresponding to the circumstance that the passages' constrictions near the walls have areas 3 to 6 times larger than within the intermeshed packing.

We shall write also

$$h_{\min} = bh_0 \tag{4}$$

with the understanding that the fact of b varies from around 3 for excellent packed columns to 6 or more for poor columns.

Since the carrier gas velocity assumed within the boundary layer is several times the velocity within the column interior, the calculation of the effect of this layer on sample diffusion can be simplified by assuming that the carrier gas in the column interior is at rest, so that the static diffusion term $2D/v$ alone operates, and by examining the effect of the velocity v_1 of the boundary layer on that static diffusion.

Within a gas mass at rest, the diffusion equation is, in cylindrical coordinates

$$D\left(\frac{\partial^2 f}{\partial x^2} + \frac{1}{r}\frac{\partial f}{\partial r} + \frac{\partial^2 f}{\partial r^2}\right) = (1 + k)\frac{\partial f}{\partial t} \tag{5}$$

where f designates the gaseous concentration of a given component and where k designates the ratio of the component mass in the fixed liquid or solid phase over the component mass in the gaseous phase. To this equation must be added the boundary condition at the interface next to the moving layer, of thickness $\frac{1}{2}h_0$,

$$\frac{2D}{r_0}\left(\frac{\partial f}{\partial r}\right)_{r=r_0} = -(1 + ck)\frac{h_0}{r_0}\left(\frac{\partial f}{\partial t}\right)_{r=r_0} - \frac{h_0}{r_0}v_1\left(\frac{\partial f}{\partial x}\right)_{r=r_0} \tag{6}$$

where c designates a factor smaller than unity, since the packing factor is smaller near the smooth wall. The average carrier gas velocity in the entire column is

$$\frac{h_0 v_1}{(1 + k)r_0 + (1 + ck)h_0}$$

and the change of independent variable

$$x_1 = x - \frac{h_0 v_1 t}{(1+k)r_0 + (1+ck)h_0} \tag{7}$$

will serve to establish an origin of coordinates moving with the average carrier gas velocity. When this change of variable is carried out in Eqs. (5) and (6), we obtain

$$D\left(\frac{\partial^2 f}{\partial x_1^2} + \frac{1}{r}\frac{\partial f}{\partial r} + \frac{\partial^2 f}{\partial r^2}\right) = (1+k)\frac{\partial f}{\partial t} - \frac{(1+k)h_0 v_1}{(1+k)r_0 + (1+ck)h_0}\frac{\partial f}{\partial x_1} \tag{8}$$

and

$$\frac{2D}{r_0}\left(\frac{\partial f}{\partial r}\right)_{r=r_0} = -(1+ck)\frac{h_0}{r_0}\left(\frac{\partial f}{\partial t}\right)_{r=r_0} - \frac{(1+k)h_0 v_1}{(1+k)r_0 + (1+ck)h_0}\left(\frac{\partial f}{\partial x_1}\right)_{r=r_0} \tag{9}$$

Let

$$f(x_1, r, t) = \bar{f}(x_1, t) + \Delta f(x_1, r, t) \tag{10}$$

and

$$\int_0^{r_0} \Delta f \, r dr = 0 \tag{11}$$

Apply now the operator $(2/r_0^2)\int_0^{r_0} rdr$ to Eq. (8) and introduce in Eqs. (8) and (9) the change of dependent variable defined by Eqs. (10) and (11). We have

$$D\frac{\partial^2 \bar{f}}{\partial x_1^2} + \frac{2D}{r_0}\left(\frac{\partial \Delta f}{\partial r}\right)_{r=r_0} = (1+k)\frac{\partial \bar{f}}{\partial t} - \frac{(1+k)h_0 v_1}{(1+k)r_0 + (1+ck)h_0}\frac{\partial \bar{f}}{\partial x_1} \tag{12}$$

and

$$\frac{2D}{r_0}\left(\frac{\partial \Delta f}{\partial r}\right)_{r=r_0} = -(1+ck)\frac{h_0}{r_0}\left[\frac{\partial \bar{f}}{\partial t} + \left(\frac{\partial \Delta f}{\partial t}\right)_{r=r_0}\right] - \frac{(1+k)h_0 v_1}{(1+k)r_0 + (1+ck)h_0}\left[\frac{\partial \bar{f}}{\partial x_1} + \left(\frac{\partial \Delta f}{\partial x_1}\right)_{r=r_0}\right] \tag{13}$$

whence, by subtraction

$$D\frac{\partial^2\bar{f}}{\partial x_1^2} = \left[(1+k) + (1+ck)\frac{h_0}{r_0}\right]\frac{\partial\bar{f}}{\partial t} + \frac{(1+k)h_0v_1}{(1+k)r_0 + (1+ck)h_0}\left(\frac{\partial\Delta f}{\partial x_1}\right)_{r=r_0} \tag{14}$$

where the term in $\partial\Delta f/\partial t$ has been neglected against the similar term $\partial\bar{f}/\partial t$, which is much larger after diffusion has proceeded for some time, as will be seen.

An approximate value for Δf is now obtained as follows. Introduce first in Eq. (8) the change of variables defined by Eqs. (10) and (11), and neglect again the terms in Δf against similar terms in $\bar{f}$, to obtain

$$D\left(\frac{\partial^2\bar{f}}{\partial x_1^2} + \frac{1}{r}\frac{\partial\Delta f}{\partial r} + \frac{\partial^2\Delta f}{\partial r^2}\right) = (1+k)\frac{\partial\bar{f}}{\partial t} - \frac{(1+k)h_0v_1}{(1+k)r_0 + (1+ck)h_0}\frac{\partial\bar{f}}{\partial x_1} \tag{15}$$

Subtract Eq. (14) from Eq. (15), and neglect again the term in Δf against the similar term in $\bar{f}$. Furthermore, neglect the term in $\partial\bar{f}/\partial t$ against the term in $\partial\bar{f}/\partial x_1$. It will be seen shortly that this last step is specifically permitted, after diffusion has proceeded for some time, by the change of independent variable defined by Eq (7) which makes the new origin travel at the speed of the component packet, so that a quasi-static diffusion equation will be obtained eventually. We have:

$$D\left(\frac{1}{r}\frac{\partial\Delta f}{\partial r} + \frac{\partial^2\Delta f}{\partial r^2}\right) = -\frac{(1+k)h_0v_1}{(1+k)r_0 + (1+ck)h_0}\frac{\partial\bar{f}}{\partial x_1} \tag{16}$$

whence, recalling Eq. (11), and stipulating that no solution should be infinite at $r = 0$

$$\Delta f = \frac{1}{4D}\frac{(1+k)h_0v_1}{(1+k)r_0 + (1+ck)h_0}\left(\frac{r_0^2}{2} - r^2\right)\frac{\partial\bar{f}}{\partial x_1} \tag{17}$$

Substitution in Eq. (14) of this value for Δf yields

$$\left[D + \frac{(1+k)^2r_0^2h_0^2v_1^2}{8D[(1+k)r_0 + (1+ck)h_0]^2}\right]\frac{\partial^2\bar{f}}{\partial x_1^2} = \left[1 + k + (1+ck)\frac{h_0}{r_0}\right]\frac{\partial\bar{f}}{\partial t} \tag{18}$$

Equation (18) is the quasi-static diffusion equation referred to above. When written in the form

$$D_1\frac{\partial^2\bar{f}}{\partial x_1^2} = \frac{\partial\bar{f}}{\partial t} \tag{19}$$

its general solution for a component packet inserted at time $t = 0$ is of the form

$$\bar{f} = \frac{1}{\sqrt{t}}\, e^{\frac{-x_1^2}{4Dt}} \tag{20}$$

and it can be easily verified from this solution that the several simplifications adopted earlier were indeed justified after diffusion has proceeded for some time.

Equation (18) indicates that the fast-moving boundary layer causes an effective increase in the static diffusion term represented by the second term within the brackets. When $r_0 \gg h_0$, the bracketed terms of the left-hand side may be written

$$D + \frac{h_0^2 v_1^2}{8D} = D + \frac{a^2 h_{\min}^2 v^2}{8b^2 D} \tag{21}$$

and substitution of this quantity in the first term of the right-hand side of Eq. (1) finally yields

$$h = 2\frac{D}{v} + \left(1 + \frac{a^2}{b^2}\right)\frac{h_{\min}^2 v^2}{8D} \tag{22}$$

It will be noted that the increase in h due to the boundary layer is essentially independent of r_0 when $r_0 \gg h_0$. It will be noted also that when a and b are of the same order of magnitude, the effect of the boundary layer is to give an optimum velocity around 0.7 times the intrinsic optimum velocity, while the HETP then obtained is around 1.4 times the intrinsic HETP, $h_{\min}$. This circumstance suggests that some benefit might be realized by using columns the inside walls of which have been roughened or grooved in order to inhibit any rapidly moving boundary layer. This precaution should be the more beneficial the smaller b is, i.e., the better the unmodified columns are.

SYSTEMATIC COLUMN INHOMOGENEITIES

Consider now a large column, characterized by a lateral dimension d, across which there is a systematic variation in the sense that while component molecules travel a distance x on one side of the column, identical molecules travel a distance $(1 + \epsilon)x$ on the other side. Were it not for sideways diffusion, the second moment of a component packet would increase quadratically with the packet's travel, but because of sideways diffusion it will be permitted to consider that the packet spreads linearly only for the distance traveled in the time during which sideways diffusion causes the molecules to diffuse the distance d. That travel distance is d^2v/D and the order of magnitude of the incremental HETP due to that effect alone can be written

$$h_1 = \frac{\epsilon^2 d^2 v}{D} \tag{23}$$

The total HETP is then given by

$$h^* = h + h_1 = 2\frac{D}{v} + \frac{h_{\mathrm{min}}^2 v}{8D} + \frac{\epsilon^2 d^2 v}{D} \tag{24}$$

where the boundary layer effect studied earlier has been neglected. Henceforth the third term of the right-hand side will be assumed much larger than the second

$$\epsilon d \gg h_{\mathrm{min}} \tag{25}$$

When v is optimized in Eq. (18), we shall have, neglecting the second term of the right-hand side,

$$h_{\mathrm{min}} = 2\sqrt{2}\epsilon d \tag{26}$$

Assume now that, instead of allowing the component packet to suffer the full incremental spread due to the additional HETP h_1, mixing washers are interposed across the column at intervals L, where

$$L < \frac{d^2 v}{D} \tag{27}$$

These mixing washers may be imagined to consist of two funneling assemblies designed to collect the gas stream uniformly across the column cross section, and assembled back-to-back with their necks connected by a coiled tubing of a certain length L_1 and diameter d_1. It is evident that for effective mixing of the gas stream within the connecting tube the time of passage of the molecules in that tube should be sufficient to permit any molecule to diffuse across it. This time is of the order of

$$t_1 = \frac{d_1^2}{D} \tag{28}$$

Within the mixing tube the gas has a velocity of the order:

$$v_1 = \frac{d^2}{d_1^2} v \tag{29}$$

(neglecting the lowered cross section of the packed tube due to the packing granules). The condition just stated for effective packing requires that the length of the mixing tube be

$$L_1 = t_1 v_1 = \frac{d^2 v}{D} \tag{30}$$

The minimum effective mixing tube length is thus seen to be independent of the tube diameter, and to be of the order of magnitude of the length of column over which molecules will diffuse sideways across the column.

Let U designate the volumetric second moment of a component packet flowing in a tube of cross section S. We have

$$U = S^2 u \tag{31}$$

where u designates the specific second moment of the packet, connected with the HETP through the relation

$$\text{HETP} = \frac{du}{dx} \tag{32}$$

The volumetric second moment has the property of being an invariant of the component packet when the gas stream follows paths of varying cross sections and when pressure changes may be neglected. During its travel through the mixing tube, the component packet suffers an incremental second moment U_2 equal to*

$$U_2 = (\tfrac{1}{4}\pi\, d_1^2)^2 \left(2\frac{D}{v_1} + \frac{d_1^2 v_1}{96D}\right) L_1 \tag{33}$$

Substituting for v_1 and L_1 their values given by Eqs. (29) and (30), and dividing by the square of the cross-section area of the column (again neglecting the occupancy of the packing grains) times the length L between washers, we obtain the contribution h_2 of the mixing tube to the effective HETP of the column

$$h_2 = \frac{U_2}{(\tfrac{1}{4}\pi\, d^2)^2 L} = 2\frac{d_1^6}{d^4 L} + \frac{d_1^4 v^2}{96D^2 L} \tag{34}$$

When v is of the order of $4D/h_{\min}$, and when $h_{\min} < d$ and $d_1 < d$, the first term of the right-hand side is negligible, and we obtain for the over-all effective HETP of the column

$$h^{**} = h + h_1 + h_2 = 2\frac{D}{v} + \epsilon^2 L + \frac{d_1^4 v^2}{96D^2 L} \tag{35}$$

when

$$L = L_{\text{opt}} = \frac{d_1^2 v}{\sqrt{96}\,\epsilon D} \tag{36}$$

we obtain

$$h^{**}_{\min} = 2\frac{D}{v} + \frac{\epsilon\, d_1^2 v}{\sqrt{24}\,D} \tag{37}$$

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* Formula (31), for $k = 0$, of my article (*3*).

and when v is optimized we obtain

$$h^{**}_{\min\,\min} = 2\sqrt{\frac{\epsilon}{\sqrt{6}}}\,d_1 \tag{38}$$

Comparison of Eq. (36) with Eq. (24) indicates that the column with mixing washers will be more efficient than the plain column if:

$$d_1 < \sqrt{2\sqrt{6}\,\epsilon}\,d \tag{39}$$

If it is stipulated that d_1 should be so selected that the pneumatic resistance of the mixing tube be equal to that of a column portion between two mixing washers, a characteristic granular dimension h_0 should be first defined, such that the resistance of the column will be the same as if it were composed of several capillaries of diameter h_0 connected in parallel, while their combined cross section is equal to that of the column.

With this convention about the average passage size of the column, the stipulation that the column and mixing tube resistances be the same can be written

$$\frac{L}{h_0^2\,d^2} = \frac{L_1}{d_1^4} \tag{40}$$

wherefrom, after substituting for L_1 its value from Eq. (30)

$$d_1^4 = \frac{d^4 h_0^2 v}{DL} \tag{41}$$

The new value for the effective HETP is now

$$h^{\dagger} = 2\frac{D}{v} + \epsilon^2 L + \frac{d^4 h_0^2 v^3}{96 D^3 L^2} \tag{42}$$

Optimization of L gives

$$h^{\dagger}_{\min} = 2\frac{D}{v} + \frac{1}{4}\left(\frac{9}{2}\epsilon^4 d^4 h_0^2\right)^{1/3}\frac{v}{D} \tag{43}$$

and optimization of v gives further

$$h^{\dagger}_{\min\,\min} = (6\epsilon^2 d^2 h_0)^{1/3} \tag{44}$$

Comparison with Eq. (25) indicates now that the use of mixing washers will be beneficial if

$$h_0 < \frac{8\sqrt{2}}{3}\epsilon d \tag{45}$$

Since h_0 is known to be appreciably smaller than $h_{\min}$, it follows that when the inequality of Eq. (25) is satisfied, Eq. (45) will be amply satisfied.

It is concluded that mixing washers will be beneficial in large preparative columns in which Eq. (25) is satisfied, i.e., in columns in which systematic variations across the columns cause an appreciable HETP increase.

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CHAPTER III

Chromatographic Solid Support Studies

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The practical value of gas chromatography has led to studies of various factors affecting chromatographic action. The effect of the solvent has been widely discussed as related to solubility parameters such as activity coefficients and relative volatilities (*1*, *2*). Effects of apparatus geometry have recently received rather thorough treatment (*3*).

The purpose of this study was to examine the effect of various solid support physical characteristics such as surface area, pore volume, pore size distribution, and particle size on column efficiency. By correlating efficiency with these physical characteristics, a description of a solid support giving optimum efficiency can be evolved. To avoid purely solvent parameter changes, the column liquid substrate throughout the study was diethylhexyl sebecate. All chromatograms were run with a Perkin-Elmer model 154 gas chromatograph using a 1-cc sample volume at 25°C. The column efficiency defined as the length of a theoretical plate, HETP, was the ratio of the column length to number of theoretical plates. The number of theoretical plates is calculated from experimental data by the equation

$$N = (4\,x/y)^2 \tag{1}$$

where x is the elution time and y is the band width.

The van Deemter equation (*4*),

$$\mathrm{HETP} = 2\lambda d_p + 2\,\frac{\gamma D_{\mathrm{gas}}}{\mu} + \frac{8}{\pi 2}\,\frac{k'}{(1 + k')^2}\,\frac{d_f{}^2}{D_{\mathrm{liq}}}\,u \tag{2}$$

states HETP as a function of packing irregularity, particle diameter, tortuosity, gaseous diffusivity, linear velocity, mass transfer and molecular diffusivity within the liquid.

The first term on the right side of Eq. (2) is related to the eddy diffusion, the second term to molecular diffusion, and the third term to mass transfer.

The surface area, pore volume, absolute density, packed density, and fractional void space of four solid support materials are listed in Table I. The surface areas were first determined by gas adsorption (B.E.T.) meth-

TABLE I

Physical Characteristics of Various Solid Supports

Type	Surface area, m^2/gm	Pore volume, cc/gm	Absolute density, gm/cc	Packed density, gm/cc	Fractional void space
J-M Chromosorb-R	4.8	1.1	2.26	0.40	0.447
J-M Chromosorb-W	1.2	2.78	2.20	0.20	0.56
J-M Celite C-29924	0.45	0.80	2.30	0.40	0.40
Beckman Teflon	0.64	0.40	—	0.73	—

ods. Comparison of such results with surface areas calculated from the pore size distribution data (assuming cylindrical pores so that $S = 4$ volume/diameter) prove the latter method of surface area determination to be accurate in all cases in which the pore size distribution is accurately known. The pore volumes and absolute densities in Table I were measured by helium-mercury displacement techniques.

Johns-Manville red chromosorb was analyzed for Al, Fe, and Ca with the following results: Al, 3.16%; Fe, 0.83%; Ca, 0.41%. Red chromosorb has considerable adsorptivity for polar materials, as HCl. The indicated presence of aluminum, probably as oxide, may be the major reason for this.

In the usual method for preparing a gas-liquid partitioning column the oil is dissolved in a volatile solvent and slurried with the solid support. The solvent is subsequently evaporated, leaving the oil deposited within the pores of the solid support particles. In order to examine the oil penetration of the air-filled fine pores three batches of column material were prepared. The first was prepared in the normal manner at atmospheric pressure as described above. The second batch was prepared by evacuating the solid support before and during the addition of the oil-solvent solution. The oil-solvent solution of the third batch was added to the evacuated solid support, then the slurry was pressured to two atmospheres. Columns prepared of these materials showed no detectable differences in chromatographic action indicating the oil was similarly located in all cases. Since this oil wets the support the fine pores in these materials were presumably filled with oil in all cases.

This was further proven in pore size distribution studies. The pore size distributions of several chromatographic materials were determined by an Aminco Wilson mercury porosimeter. Figure 1 shows the pore size distribution of red chromosorb with 0, 5, 10, 20, and 33% by weight oil. The majority of the pores in oil-free chromosorb are between 0.4 and 2 μ diameter. As the oil was added it selectively filled the finest available pores. Within the experimental accuracy of the measurements, the observed loss in pore

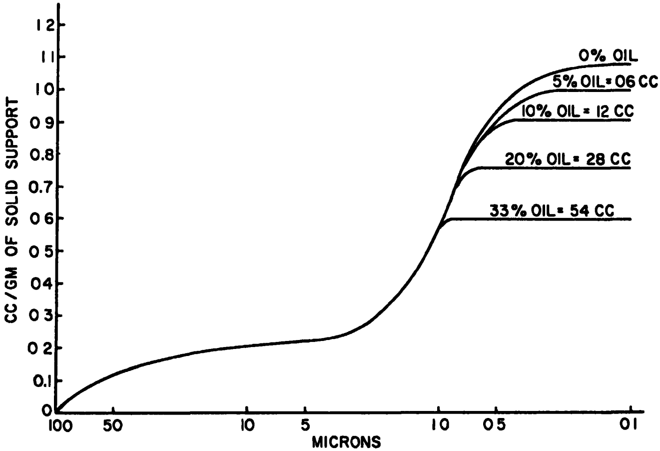

FIG 1 Pore size distribution: red chromosorb, dry and with oil.

volume was equal to the volume of oil added. This indicates that most of the oil is located in the finest available pore structure of the particle with a thin oil film over the remainder of the surface.

The pore size distribution of Johns-Manville Celite C-29924, porous Teflon, and a special preparation of chromosorb is presented in Fig. 2. The special chromosorb has the same type of pore structure as plain chromosorb except the former has almost no pores of less than 1 μ diameter. The Celite C-29924 pores are mostly 10 to 50 μ in diameter with practically no pores less than 1.5 μ. By preparing columns of these materials having equal volumes of oil per unit volume of column, experimental evidence of the effect of pore size is obtained.

Figure 3 is a plot of HETP versus gm/ft of oil in the column for red chromosorb, the special chromosorb, and Celite C-29924. Each curve exhibits a minimum HETP, indicating an optimum oil concentration with this optimum occurring at lower concentrations as the fine pore structure is reduced. The slopes of the curves on either side of the minimum become much steeper with a decrease in the fine pore structure. The oil concentration is, therefore, far more critical for solid supports having fewer fine pores. It would be interesting to examine a solid support material having a large quantity of pores in 0.1 μ range, but a material of this description was not available at the time of these studies.

As has been previously stated, HETP is calculated from experimental data by the relationship

$$\text{HETP} = \frac{L}{\left(4\frac{x}{y}\right)^2} \tag{3}$$

Thus, HETP varies directly with y^2 and $1/x^2$. In order to obtain a clearer understanding of the method in which HETP varies with oil concentration,

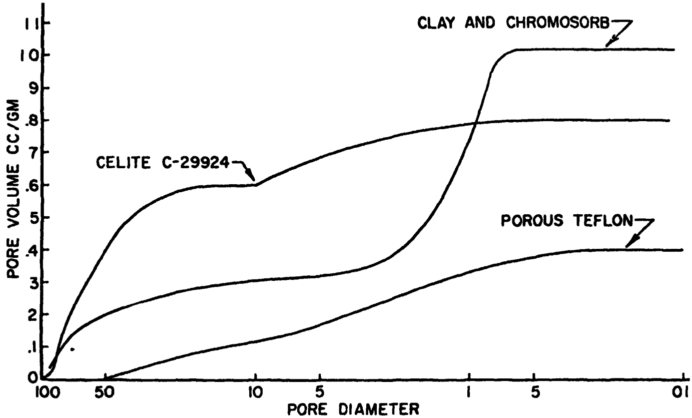

FIG 2. Pore size distribution: Celite, Teflon, and a special preparation of chromosorb.

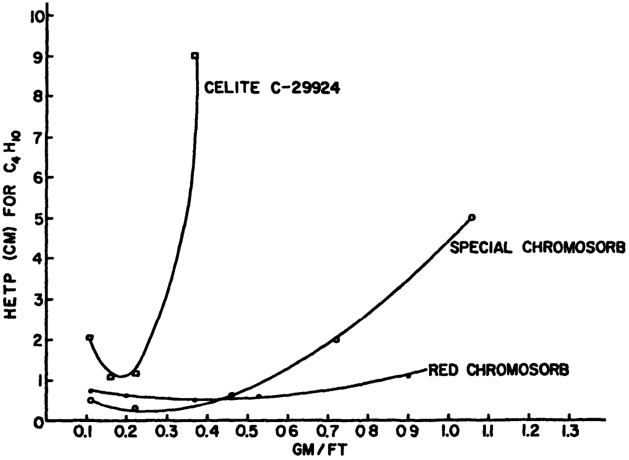

FIG. 3. Substrate oil concentration.

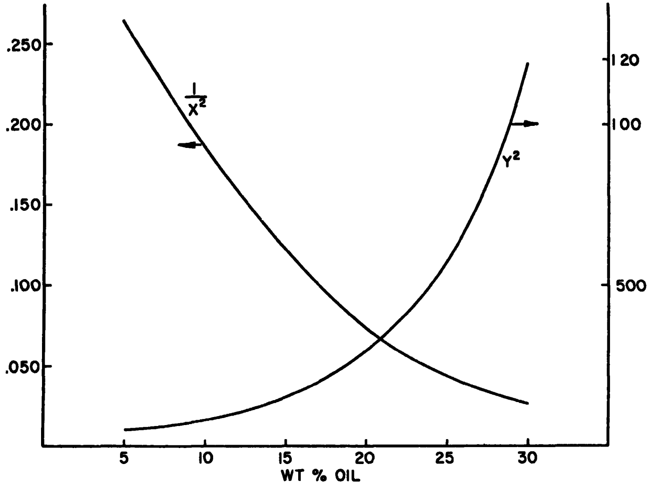

Fig 4 Plot of y^2 and $1/x^2$ vs. oil concentration on red chromosorb

y^2 and $1/x^2$ are plotted against oil concentration on red chromosorb in Fig. 4. The $1/x^2$ function is a rather flat descending curve almost linear to 20% oil and gradually curving to approach the ordinate asymptotically at higher concentrations. The y^2 function shows a gradual rise to about 15% oil, then curves sharply upward. The HETP curve thus diminishes initially as the oil concentration increases because the column is experiencing the greatest change in elution time and the least band spreading. As the oil increases above 15% the effect of elution time change becomes almost negligible while that of band spreading rapidly becomes more dominant.

Examination of the y^2 and $1/x^2$ functions for the other materials shown in Fig 3 reveals the $1/x^2$ curves to be virtually identical to that of red chromosorb, while the y^2 curves bend upward more sharply at lower oil concentrations for those materials having less fine pore structure. Since the $1/x^2$ curves are similar for all materials, the apparent activity coefficient of the oil-sample system is unchanged. This indicates that, within the range of pore sizes tested, there is no great change in thermodynamic properties of the oil in the pores.

As is indicated by the behavior of the y^2 curve, the presence of oil in larger amounts than some given optimum causes considerable band spreading. Solid supports with relatively less fine pore structures have a lower optimum oil concentration and the band spreading above the optimum is more severe than exhibited by solid supports with relatively more fine pore structures. Consideration of differences in the location and condition of the oil should lead to some clue as to the rate-determining step of the chromatograph process at high oil concentrations. The most obvious difference between oil in fine pores and oil in the large pores is the size of the individual oil pools. The sample molecules must diffuse through the open pores, cross the gas-liquid interface, diffuse into the oil, return to and cross the liquid-gas interface, and diffuse out through the open pores.

The rate of gaseous diffusion of the sample molecules through the open pores of the solid support particles possibly could, if rate-controlling, cause considerable band spreading. The effect of oil on the rate of diffusion of several gases through the pores of red chromosorb was measured at several oil concentrations. Each chromosorb particle was of regular geometric form having a uniform cross-sectional area. The particles were molded in a plastic cylinder with the main axis of each aligned with the main axis of the cylinder. The chromosorb was exposed at either face of the cylinder, providing a gas flow path through the chromosorb with no gas slippage down the sides of the particles possible. The diffusion rates of various gases through these chromosorb-oil samples were measured as described by Weisz and Prater (*5*). The measured diffusion rate in cm^2/sec of hydrogen is plotted against oil concentration in Fig. 5. The diffusion rates of several hydrocarbons at various oil concentrations are given in Table II, the starred values being both experimentally determined and calculated by the rela-

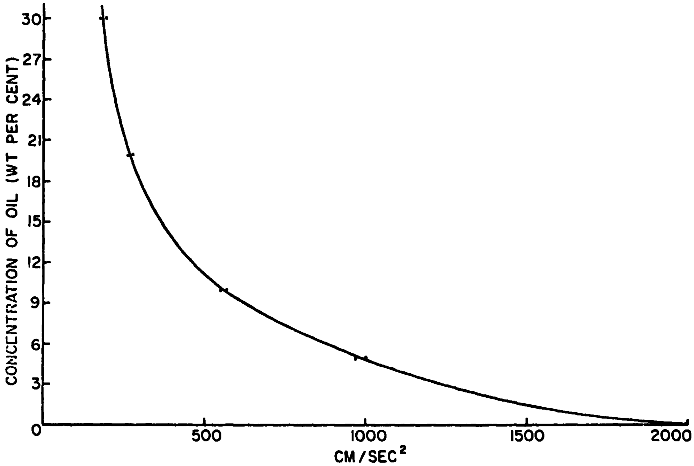

FIG 5 Diffusion rate of H_2 through red chromosorb.

TABLE II

DIFFUSION RATES (cm²/sec)

Oil concentration, weight %	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
0	446	437	388	379*	341	313
5	220	216*	191*	187*	169	154
10	120	118*	105	102*	92	84
30	44.2	43	38.5	37.6*	34	31

* Experimentally determined and calculated by the relationship $D = kM^{-1/2}$, where k is a proportionality constant, M is the molecular weight, and found to agree within ±3%

tionship $D = kM^{-1/2}$, where k is a proportionality constant, M is the molecular weight *(6)*, and found to agree within ±3%.

As can be seen in Fig. 5, the gas diffusion rate decreases rapidly with addition of oil in the low concentration range, but changes become relatively insignificant at oil concentrations above 15%. This is as anticipated if the effect of oil on diffusion rate through the pores is simply the effect of sealing off pores. However, HETP is observed to change considerably with addition of oil in the 15–30% region. It is concluded that the gas diffusion rate does not control or even contribute significantly to the increased band spreading observed with increased oil.

Since the band spreading is not controlled by gaseous diffusion in the pores, it is apparently controlled by mass transfer between the oil and gas phases, including transfer across the interface and diffusion of the solute within the liquid. Larger pools of oil, resulting from larger pores, would be deeper, hence would require longer transit times for the solute molecules within the liquid. Diffusion of the gas within the liquid probably contributes to the control of the band spreading. The larger pools, being deeper, would be expected to have a smaller surface to volume ratio. Because of this the average transfer across the interface rate per volume of oil would be slower for material having large diameter pores than for those having small diameter pores. The transfer across the interface is very likely to be the principal rate-controlling step. The present evidence does not prove this but does tend to support this conclusion.

A study of the effect of support particle size on chromatographic action was made using columns prepared from closely sized red chromosorb particles. The particle ranges employed were 35–40, 40–45, 50–60, 100-120, and 140–200 mesh corresponding to an average particle size of 460, 385,

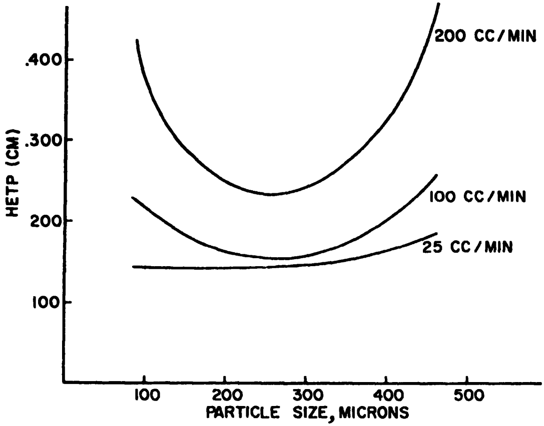

FIG. 6 Plot of HETP vs. particle size for n-C_4H_{10}.

274, 143, and 81 μ, respectively. Each material was prepared with 20% by weight oil. Each 6-ft column was carefully packed and the measured packing densities showed a deviation of +2% over all columns prepared. One-cc samples of 5% n-C_4H_{10} and 5% n-C_5H_{12} in hydrogen were run with each column at hydrogen carrier flows of 25, 100, and 200 cc/min and the resulting HETP's calculated.

Figure 6 is the plot of HETP versus particle size for n-C_4H_{10}. The n-C_5H_{12} curves were similar but lay slightly lower as expected. The curves showed a minimum at particle sizes around 275 μ. It was noted that when the HETP values for both compounds were normalized for differences in gas diffusion rates, their 25-cc/min carrier flow curves coincide. The normalized HETP curves for both components for higher flows coincide for all particle sizes less than 275 μ but diverge at larger particle sizes.

The variations in $1/x^2$ and y^2 with particle size at the 200-cc/min flow are shown in Fig. 7. The $1/x^2$ curve initially shows a fairly gentle positive slope with increased particle sizes, bends at around 275 μ and gives a slight negative slope with larger particles. This would give rise to a variation of apparent activity coefficients of the oil-solute system with particle size. The y^2 curve passes through a minimum at around 275 μ and appears to curve upward sharply at both larger and smaller particle sizes. As the particle size approaches zero the y^2 value would appear to be approaching infinity. Clearly the band spreading would become much worse for very large or very small particles.

Figure 8 is a plot of the HETP against the average time required for a

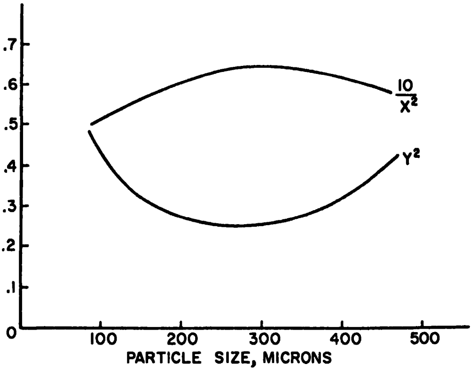

FIG. 7. Variations in $1/x^2$ and y^2 curves with particle size at the 200 cc/min flow.

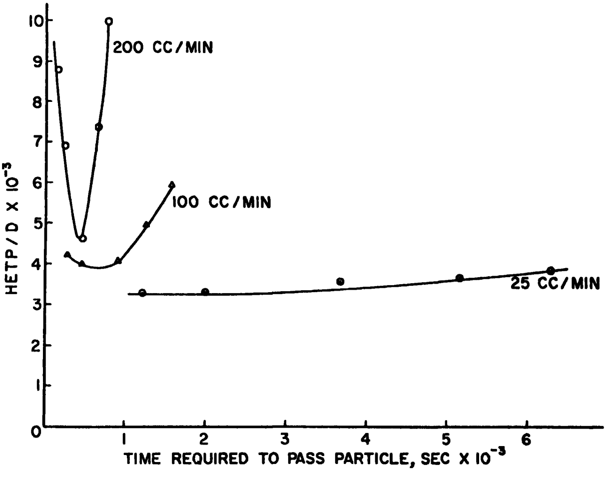

FIG 8 Plot of HETP vs. average time required for a point to pass the particle.

point to pass the particle. The average time to pass a particle is given by the relationship $t = dia/u$, where *dia* is the average particle diameter and u is the linear velocity. The linear velocity can be calculated by the relationship

$$u = F_cLT/V_cV_F$$

The average column flow rate F_c is the effluent carrier flow rate corrected for column pressure drop effects. V_c is the empty column volume, V_f is the fractional void space. The tortuosity factor T may be evaluated by assuming an average flow path at 45° angle to the longitudinal axis of the column. This would give an average path length greater than the column length by a factor of $\sqrt{2}$. Thus T is taken to equal 1.4.

As can be seen in Fig. 8, the relatively flat curve for the 25-cc/min flow does not extend into the region where a noticeable increase in HETP would be expected. Unfortunately, columns of still smaller average particle sizes were not available for this study. It remains to be seen if the HETP value for 25-cc/min flow would increase appreciably at smaller particle sizes. The curves for higher flows exhibit minima which become sharper and more toward the left as the flow is increased.

If the diffusional and mass transfer terms are neglected the van Deemter equation relates HETP and particle size as

$$\text{HETP} = 2\lambda\, dp$$

where λ is the packing irregularity factor and dp is the particle diameter. Keulemans and Kawantes (*4*) calculated λ to vary from 1 for the largest particles to 8 for the smallest particles of this study. This gives a calculated minimum at approximately 300 μ particle diameter rather than the 275 μ observed. It should be noted that this calculation gives HETP values the magnitude of 0.05 cm if all other terms of the van Deemter equation are assumed to be zero. The observed values were approximately one order of magnitude greater than this. Since the remaining terms of the van Deemter equation are independent of particle size, the observed minimum is not completely accounted for.

The results of Fig. 6 do not appear to conflict appreciably with those reported by Purnell (*6*) but are in rather good agreement over the experimental range covered by both sets of experiments. The present study extends to smaller particles and higher flows and it is in these regions that the greatest changes are observed. A definite need for a closer study of the effect of particle size is indicated by the present results.

Although there appears to be a need for considerable further investigation of the role of solid supports in chromatographic action, a tentative general description of optimum solid supports can be made at this time. Since sizing is important to column efficiency a solid support of hard material which will not undergo excessive attrition with normal handling is desirable. Chemical and sorption effects of the solid support on the sample components must be at a minimum for gas-liquid chromatographic uses.

The pore size appears to be the most important solid support physical property affecting the performance of a chromatographic column. While the optimum pore size is undetermined at this time, a solid support having a pore structure of fairly uniform pore diameter in the range of 1 micron or less, possibly much less, is indicated. The volume of the fine pore structure need only be large enough to contain significant quantities of oil to avoid crowding of the oil into any large pores present.

The size of the solid support particle is clearly important to the column efficiency. It is generally agreed that close sizing of the particles is desirable. There remains, however, some disagreement as to the optimum particle size. The evidence of the present study indicate the optimum size to be 275-300 μ, particularly if carrier flows of the order of 100 cc/min or higher are employed. Presumably it would be desirable to have regular shaped particles to minimize packing irregularity effects.

Solid support materials which more nearly fit the above description may now be available or possibly can be made available. It is to be hoped that such materials will come to the attention of those working in the art.

SUMMARY

This study relates physical properties such as pore volume, pore size distribution, surface area and particle diameter with column efficiency of a gas chromatograph. The location and condition of the liquid phase on the solid support is discussed. A preliminary description of the physical properties of an optimal solid support has been given.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Dr D T Oakes, of the Monsanto Chemical Company, who prepared the above-mentioned special chromosorb sample

LIST OF SYMBOLS

D	Diffusion rate of gas through porous material, cm²/sec
D_{gas}	Molecular diffusivity in gas
D_{liq}	Molecular diffusivity in liquid
d_f	Statistical average liquid film thickness.
d_p	Particle diameter
F_c	Average gas flow rate through column
HETP	Height equivalent to a theoretical plate
k'	Equivalent to extraction coefficient
L	Length of column
M	Molecular weight
T	Tortuosity, $T = 1\ 4$
u	Linear gas velocity
V_F	Fractional void space of column
V_c	Empty column volume
x	Elution time
y	Band width time
γ	Tortuosity factor.
λ	Measure of packing irregularities

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CHAPTER IV

A Solid Support for the Gas-Liquid Chromatography of Strongly Basic Nitrogen Compounds

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A solid support has been developed for the gas-liquid chromatography of nitrogen compounds of pK_a range 6–11. The support was obtained by depositing 10 gm of potassium hydroxide on 100 gm of the solid support recently developed by the authors for the analysis of pyridines (*1*). The modified support gave symmetric peaks for 13 nitrogen compounds in the pK_a range studied when nonpolar liquid substrates were used. This support allows the use of nonpolar liquid substrates for the analysis of basic compounds.

The solid support recently developed for the analysis of pyridines was a porous inorganic solid prepared from a commercial detergent. The solid support, while excellent for analysis of pyridines, could not be used for nitrogen compounds more basic than pyridines due to the asymmetric peaks obtained.

EQUIPMENT AND MATERIALS

Apparatus

The gas-liquid chromatographic apparatus was assembled in this laboratory and consisted of a thermistor-type detector and chromatographic column in a thermostatically controlled, stirred air bath. The temperature was maintained at 100 ± 0.5°C. Helium, regulated to a flow rate of 60.0 ± 0.1 ml/min, was used as the carrier gas.

The chromatographic columns were prepared by filling 2.5 meters of ¼-inch aluminum tubing with the packing. Glass wool was placed in each end of the column which was then coiled and fitted to the detector in the stirred air bath.

Solid Support

A commercial detergent (Tide) was crushed on a 40-mesh screen with a pestle, using a gentle motion. The material passing the screen was resieved and the 40- to 60-mesh fraction was heated at 140°C and 100–200 mm Hg pressure for 20 hours. This material was again sieved and the 40- to 60-mesh

TABLE I

MATERIALS USED AS LIQUID SUBSTRATES

Nonpolar	Polar
Apiezon-L	Monohydroxyethyltrihydroxypropylethylenediamine
Mineral oil	Tetraethylene glycol
Squalane	
Silicone oil, D C 703	

fraction was extracted with petroleum ether in a Soxhlet extractor. The porous residue from the thimble was heated at 110°C for 1 hour in an explosion-proof oven to remove the petroleum ether. Ten grams of potassium hydroxide was then deposited on 100 gm of the porous solid by pouring the solid into a methanolic solution of potassium hydroxide. The solid was heated in an explosion-proof oven as before to remove the methanol. The resulting solid was employed as the support for the liquid substrates.

Liquid Substrates

The liquid substrates used are listed in Table I. Four of these are representative of the commonly used nonpolar substrates. Monohydroxyethyltrihydroxypropylethylenediamine and tetraethylene glycol were included as representatives of the polar class of substrates.

Preparation of Packings

The hydroxide-treated solid was used as a support for the liquid substrates. The substrate was dissolved in a quantity of petroleum ether or acetone to give a ratio of 20 gm of substrate per 100 gm of solid. The solid was added to the solution and most of the solvent was removed by evaporation, while the mixture was gently stirred. The packing was heated at 110°C for 1 hour for final removal of solvent, it was sieved and the 40- to 60-mesh fraction was used to pack each column. The packing prepared in this way was granular and free-flowing and appeared dry.

Test Compounds

The compounds, listed according to boiling point in Table II, were used to test each packing. The nitrogen compounds are from several classes of basic compounds in a pK_a range of approximately 6–11. The two hydrocarbons were used as reference compounds.

EXPERIMENTAL PROCEDURES AND RESULTS

The compounds listed in Table II were run over packings prepared by using the substrates in Table I and the 10% potassium hydroxide support.

TABLE II

TEST COMPOUNDS

Compound	Approximate bp, °C	pK_a
	Basic Nitrogen Compounds	
n-Propylamine	49	10.53[a]
n-Butylamine	78	10.59[a]
1-Methylpyrrolidine	82	10.46[a]
Pyrrolidine	89	11.27[a]
n-Pentylamine	104	10.6[b]
Piperidine	106	11.22[a]
2-Methylpiperidine	118	11.2[b]
2,6-Dimethylpiperidine	126	11.2[b]
2-Methylpyridine	129	5.95[c]
1-Ethylpiperidine	131	10.1[b]
n-Hexylamine	133	10.6[b]
2,6-Dimethylpyridine	144	6.72[c]
2-Ethylpyridine	149	6.0[b]
	Hydrocarbons	
n-Heptane	98	—
Ethylbenzene	136	—

[a] From Hall (*2*)

[b] Estimated.

[c] From Ikegawa *et al* (*3*)

The compounds were run both individually and in mixtures. Figures 1 and 2 show chromatograms obtained when an 8-component mixture was run over two nonpolar liquid substrates. The degree of symmetry of the peaks was used as a measure of the extent of interaction of the solid support and sample vapors. The symmetries of the peaks for the basic nitrogen compounds were as good as those for the reference hydrocarbons, indicating that there was negligible interaction between the basic compounds and the solid support. The peaks obtained for all of the test compounds when run over squalane, mineral oil, Apiezon-L, and Dow Corning 703 silicone oil had symmetries equivalent to those shown in Fig. 1.

The nonpolar substrates have differences in selectivity that are useful in performing certain separations. These differences for two of the substrates are shown in Figs. 1 and 2.

The two polar liquid substrates were not as useful as the nonpolar substrates. Some classes of the basic compounds apparently interacted with the polar substrates. The strongest interaction was obtained when a mixture of the *n*-alkylamines was run over the monohydroxyethyltrihydroxypropyl-

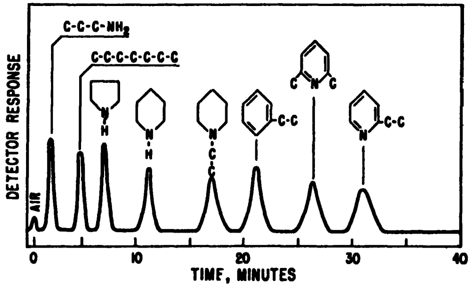

FIG. 1 Chromatogram of hydrocarbons and basic nitrogen compounds on DC 703 silicone oil, using the modified solid support.

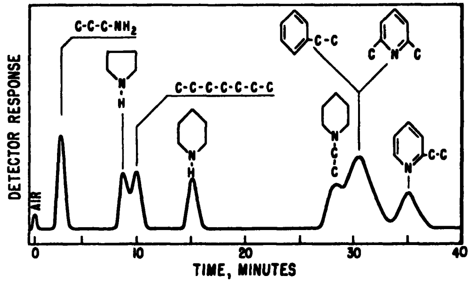

FIG. 2. Chromatogram of 8-component test mixture on squalane, using the modified solid support.

ethylenediamine packing. In this case, the peaks obtained were broad and unresolved.

The results of this work show that the potassium hydroxide-treated support together with a nonpolar liquid substrate is useful in the gas-liquid chromatography of basic nitrogen compounds. This combination gives good selectivity and peak symmetry.

DISCUSSION

The development of the modified solid support described in this work exploited the properties of a spray-dried commercial detergent to obtain a support for the analysis of strongly basic nitrogen compounds. This solid had a suitable surface area to support the desired quantity of liquid substrate and was inert, that is, it did not absorb sample vapors. In the commercial detergent, surfactants such as alkylbenzene sulfonates and alkyl

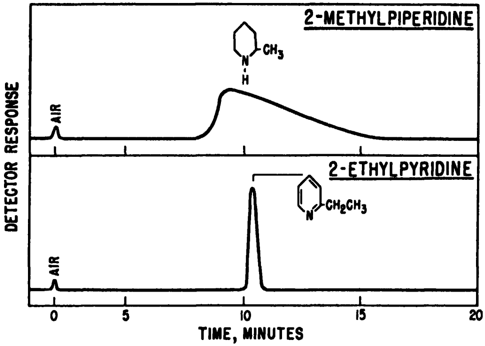

FIG. 3 Chromatograms of 2-methylpiperidine and 2-ethylpyridine on squalane, using the untreated solid support.

sulfates are intimately mixed in an inorganic matrix, which contains sodium sulfate, sodium triphosphate, sodium pyrophosphate, and sodium silicates. Heating the detergent removed water and converted insoluble surfactants to a petroleum ether-soluble form. Extraction of the heat-treated detergent with petroleum ether then removed 97 to 99% of the original surfactants. The remaining inorganic matrix was a porous, sponge-like solid and had a surface area large enough to contain a ratio of 50 gm of liquid to 100 gm of solid and still appear dry and remain free-flowing. This porous solid did not absorb pyridines, as shown by the lower chromatogram in Fig. 3, and was used in the separation of these compounds with good results (*1*). However, this material could not be used for nitrogen compounds more basic than pyridines as asymmetric peaks were obtained. This is shown by the upper chromatogram in Fig. 3.

The asymmetric peaks obtained with strongly basic nitrogen compounds may be due to chemisorption of these compounds by the solid support. Acidic residues, such as sodium bisulfate, which has been postulated (*4*) to result from the thermal decomposition of alkyl sulfates, might be the cause of this interaction. In an effort to overcome this chemisorption, 2.5, 5, and 10 gm of potassium hydroxide were deposited on each 100 gm of the solid support. As the support using 10 gm of potassium hydroxide gave symmetric peaks, the solid support used in this work was prepared to contain this quantity.

A solid support that would be generally useful in gas-liquid chromatography might be prepared from a spray-dried, simple mixture of a neutral inorganic salt, perhaps potassium chloride, and an easily removable organic compound.

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CHAPTER V

The Role of Column Backflushing in Gas Chromatography

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INTRODUCTION

Conventional analysis by gas chromatography involves injection of a sample at the head of a column and the eventual elution of its components at the column exit. Since direction of carrier gas flow and other column parameters remains unchanged, total analysis time is a function of the components involved.

Departure from this conventional pattern sometimes has distinct advantages. In this technique, flow of carrier gas is reversed, causing sample components remaining in the column to be swept back and eluted at the column inlet. Total analysis time is primarily a function of flow reversal. This technique is sometimes referred to as "backflushing" Its application to the analysis of light ends in petroleum products has been reported in the literature. (1, 2, 3)

Reduction of time per analysis was the primary advantage gained in the references cited here. Generally, backflushing is started when components of individual interest have been eluted from the column. Thus, heavier components having objectionably long retention times are removed from the column in about twice the time for the analysis of the light ends.

It should be noted that backflushing is a useful tool for what might be termed "column housecleaning." Experimenters working with new columns on samples of dubious origin would often welcome knowledge that a column is free of heavy trace components. This becomes more significant with increasing sensitivity.

Backflushed material may, in some instances, appear as a single symmetrical peak. This suggests that peak height or area could be measured and additional quantitative information could be obtained. However, application of the technique to analytical and/or control problems should not be undertaken without full awareness of the limitations imposed by column parameters and detector characteristics. Some factors which affect quantitative accuracy are: (a) differences in backflush retention times of individual components; (b) differences in relative peak width or shape; and (c) differences in detector response to individual components.

DEFINITION OF TERMS

Foreflush Mode. The normal operation of a chromatographic column, that is, the direction of carrier flow that exists at the time the sample is introduced into the column.

Backflush Mode. The operation of the column with the carrier flow reversed with respect to the foreflush mode.

Backflush Time (t_f). The time elapsed between the introduction of the sample and the reversal of the carrier flow.

Return Time (t_r). The time elapsed between the reversal of carrier flow and the emergence of a peak.

Foreflush Retention Time (t_c). The observed retention time of a peak with the column in foreflush only.

Backflush Retention Time ($t_f + t_r$). The observed retention time of a backflushed peak, i.e., the total residence time in the column.

THEORETICAL

It had been noted in preliminary work that if the boiling range of backflushed components was relatively narrow they were eluted as a single peak. If the range was quite broad, however, they would have the appearance of several partially resolved peaks. It had been further noted that even in narrow range samples the backflush retention time was unique for each component. The backflush retention time can be related to the foreflush retention time through a consideration of the existing velocity gradient. In a column of length L with inlet and outlet pressure P_i and P_o, respectively, the distance X from the inlet (or the fractional distance x) at which a pressure P_x exists, is given by:

$$x = \frac{X}{L}\,\frac{(P_i^2/P_o^2) - (P_x^2/P_o^2)}{(P_i^2/P_o^2) - 1} \qquad (1)$$

which, when rearranged, gives P_x, the pressure at x relative to the outlet pressure.

$$p_x = \frac{P_x}{P_o} = \left[\frac{P_i^2}{P_o^2} + x\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{1/2} \qquad (2)$$

The velocity (u_x) of the carrier gas at x is related to the outlet velocity (u_o)

$$u_x = \frac{u_o}{p_x} \qquad (3)$$

Assuming that at all p_x the velocity of a component (u_c) is related to the velocity of the carrier gas by a constant factor α_c (which is a function of the specific retention volume)

$$u_c = \alpha_c u_x \tag{4}$$

then

$$u_c = \frac{\alpha_c u_o}{p_x} \tag{5}$$

and

$$u_c = \frac{\alpha_c u_o}{\left[\frac{P_i^2}{P_o^2} + x\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{1/2}} \tag{6}$$

The time required for a component to travel from any point x_1 to any other point x_2 is given by the integral

$$t = \int_{x_1}^{x_2} \frac{dx}{u_c} \tag{7}$$

substituting Eq. (6)

$$t = \frac{1}{\alpha_c u_o} \int_{x_1}^{x_2} \left[\frac{P_i^2}{P_o^2} + x\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{1/2} dx \tag{8}$$

and integrating

$$t = \frac{2}{3} \frac{1}{\alpha_c u_o} \frac{1}{1 - (P_i^2/P_o^2)} \left\{\left[\frac{P_i^2}{P_o^2} + x\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{3/2}\right\}_{x_1}^{x_2} \tag{9}$$

If the integral is evaluated for $x_1 = 0$ and $x_2 = 1$, the foreflush retention time of the component is obtained.

$$t_c = \frac{2}{3} \frac{1}{\alpha_c u_o} \frac{1 - (P_i^3/P_o^3)}{1 - (P_i^2/P_o^2)} \tag{10}$$

If, however, the carrier gas flow is instantaneously reversed when the component peak has traversed only a fraction (f) of the column, the backflush time (t_f) is obtained by evaluating for $x_1 = 0$ and $x_2 = f$.

$$t_f = \frac{2}{3} \frac{1}{\alpha_c u_o} \frac{1}{1 - (P_i^2/P_o^2)} \left\{\left[\frac{P_i^2}{P_o^2} + f\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{3/2} - \frac{P_i^3}{P_o^3}\right\} \tag{11}$$

If we assume that the component peak is not displaced by reversal of carrier gas flow, then the return time (t_r), (that is, the additional time required for the component peak to return to the column inlet) is obtained by evaluating Eq. (9) for $x_1 = 1 - f$ and $x_2 = 1$,

$$t_r = \frac{2}{3} \frac{1}{\alpha_c u_o} \frac{1}{1 - (P_i^2/P_o^2)} \left\{1 - \left[1 - f\left(1 - \frac{P_i^2}{P_o^2}\right)\right]^{3/2}\right\} \tag{12}$$

the term outside of the brackets in Eqs. (11) and (12) can be eliminated by rearranging Eq. (10)

$$\frac{2}{3}\frac{1}{\alpha_c u_o}\frac{1}{1-(P_i^2/P_o^2)} = \frac{t_c}{1-(P_i^3/P_o^3)} \tag{13}$$

and substituting in Eqs. (11) and (12)

$$t_f = \frac{t_c}{1-(P_i^3/P_o^3)}\left\{\left[\frac{P_i^2}{P_o^2}+f\left(1-\frac{P_i^2}{P_o^2}\right)\right]^{3/2}-\frac{P_i^3}{P_o^3}\right\} \tag{14}$$

$$t_r = \frac{t_c}{1-(P_i^3/P_o^3)}\left\{1-\left[1-f\left(1-\frac{P_i^2}{P_o^2}\right)\right]^{3/2}\right\} \tag{15}$$

Rearranging Eq. (14)

$$f = \frac{\left[\dfrac{t_f}{t_c}\left(1-\dfrac{P_i^3}{P_o^3}\right)+\dfrac{P_i^3}{P_o^3}\right]^{2/3}-\dfrac{P_i^2}{P_o^2}}{1-(P_i^2/P_o^2)} \tag{16}$$

And substituting in Eq (15)

$$t_r = \frac{t_c\left[\left\{1+\dfrac{P_i^2}{P_o^2}-\left[\dfrac{P_i^3}{P_o^3}-\dfrac{t_f}{t_c}\left(\dfrac{P_i^3}{P_o^3}-1\right)\right]^{2/3}\right\}^{3/2}-1\right]}{(P_i^3/P_o^3)-1} \tag{17}$$

It is more illustrative if t_r/t_f [that is, $(t_r/t_c)/(t_f/t_c)$] is plotted against t_f/t_c for various values of P_i/P_o, as in Fig. 1.

EXPERIMENTAL

Backflushing was accomplished in the laboratory unit by means of a manually operated dual column valve, and in the industrial model with two standard pneumatic dual column valves. These were actuated simultaneously by an air signal from an electrically controlled solenoid valve. Liquid samples were introduced directly into the heated inlet of the laboratory unit. Vaporization was assumed to be instantaneous. A sample size of approximately 0.001 ml was used for pure components. Foreflush retention times were obtained by running a mixture containing all the components, the sample size in those cases being increased to 0.01 ml. Gaseous samples only were used with the industrial instrument. All columns were packed in tubing of ¼-inch outer diameter.

The ratio of inlet to outlet pressures was controlled primarily by adjusting the inlet pressure. Outlet pressures above atmospheric were attained by means of a variable restriction downstream of the detector.

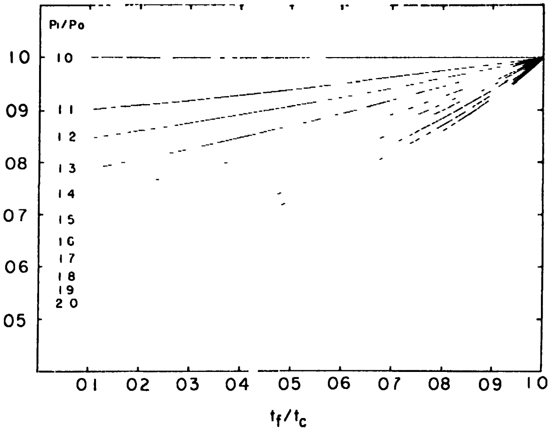

FIG 1 Relative return times of backflushed components

BACKFLUSH RETENTION TIME

Equation (17) indicates that the retention time of backflushed components is related to their foreflush retention times and the ratio of the inlet to outlet pressures, and is independent of the absolute magnitude of these pressures. The experimental values of t_r/t_f for a series of C_6–C_8 paraffins are shown in Fig. 2. For each of these two sets of runs, t_f was constant while t_c was characteristic for each compound. The results of backflushing a single compound at different times after injection are shown in Fig. 3; this was equivalent to varying t_f while holding t_c constant.

The solid lines in Figs. 2 and 3 represent the theoretical at the experimental values of P_i/P_o. In each case the backflush retention times are somewhat greater than predicted, and, in the case of Fig. 3, this disagreement becomes more severe with increasing volatility of the compound. The cause of this may be the pressure disturbances created within the column by the presence of the component as described by Van de Craats (*4*). To minimize this effect, it would be desirable to determine t_r at extrapolated zero sample size. In any event, the above manner of plotting the results tends to magnify small errors as the absolute values of t_c and t_f become smaller. The data presented in Fig. 2 can also be plotted in the more usual form of log retention time vs. boiling point. Comparison with a similar plot of the foreflush retention times serves to illustrate the observed backflushed retention times. In Fig. 4, both backflush retention times (that is, $t_r + t_f$) and foreflush retention times, corrected for dead time, have been plotted

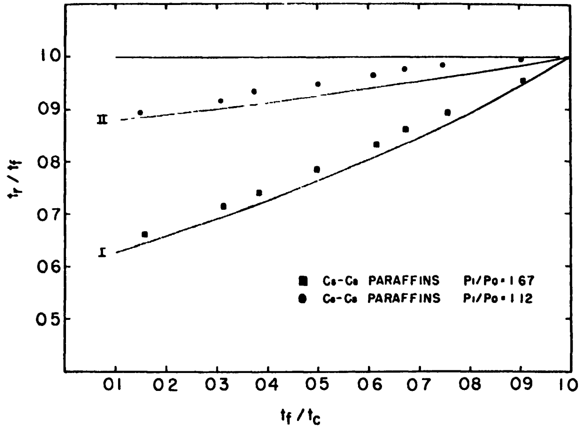

FIG. 2. Relative return times of C_6–C_8 paraffins backflushed at constant t_f . Instrument. Beckman GC-2 Gas Chromatograph; column 15 ft; packing. 30% silicone oil on 42–60 mesh C-22; helium carrier gas, temperature. 77°C.

Curve	Carrier flow, ml/min	P_i	P_o	P_i/P_o
I	55	24.2	14.5	1.67
II	55	40.1	35.9	1.12

in this manner. The solid lines represent the best fit for the theoretical backflush retention times as calculated on the basis of the observed foreflush retention times.

PEAK WIDTH

When the column was operated with the outlet at atmospheric pressure, the width of the peaks as measured at half-height seemed to be influenced primarily by their total residence time in the column. Backflushing the C_5 through C_7 *n*-paraffins at various times after being introduced into the column resulted in peak widths about the same as a foreflush peak of the same retention time, as shown in Fig. 5. The observed width is somewhat greater than would be expected on that basis for those runs in which the time at which backflushing was begun after the component was only a short distance into the column (that is, t_f/t_c equal to about 0.2). This is indicated by the experimental points at the left in each series. The plot also indicates a trend for increasing width with increasing molecular weight at a given backflush retention time.

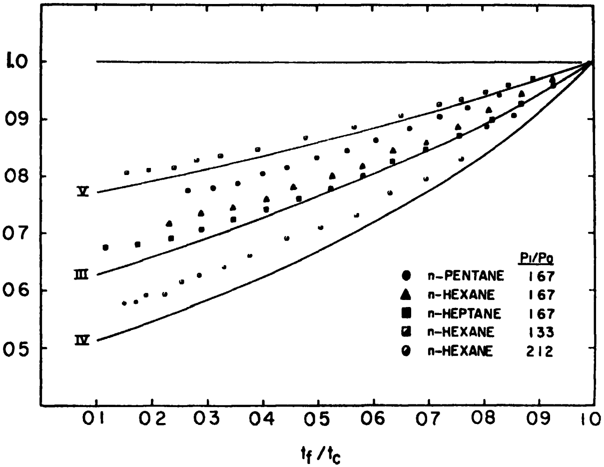

FIG. 3. Relative return times of C_5–C_7 *n* paraffins backflushed at varying t_f's Instrument: Beckman GC-2 Gas Chromatograph, column: 15 ft, packing: 30% silicone oil on 42–60 mesh C-22; helium carrier gas; temperature: 77°C

Curve	Carrier flow, ml/min	P_i	P_o	P_i/P_o
III	55	24.2	14.5	1.67
IV	107	30.7	14.5	2.12
V	27	19.3	14.5	1.33

Backflushing a series of paraffins at a given time t_f, results in a more pronounced broadening of the heavier compounds at the elevated column pressure, as shown in Fig. 6, even though the spread in relative backflush elution times is less than that at atmospheric column outlet pressure. The absolute magnitudes of the retention times at the higher outlet pressure were about twice that at the lower pressure.

DISCUSSION

Where the measurement of the backflushed components is made on the basis of peak height, the assumption is made that the height of the combined peak is equal to the sum of the individual peaks. This is, of course, true only if the retention times of the individual peaks are identical, a condition which can exist only when P_i/P_o is equal to unity. If two identical peaks are separated by approximately 0.17 times their width at half-height, the error introduced by the assumption is only 2%. The error increases to

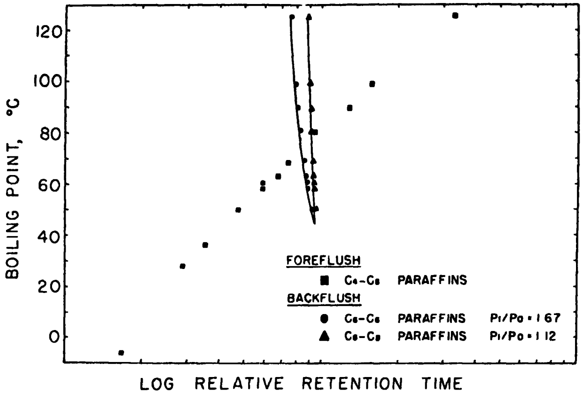

Fig 4 Log relative retention times of backflushed and foreflushed paraffins.

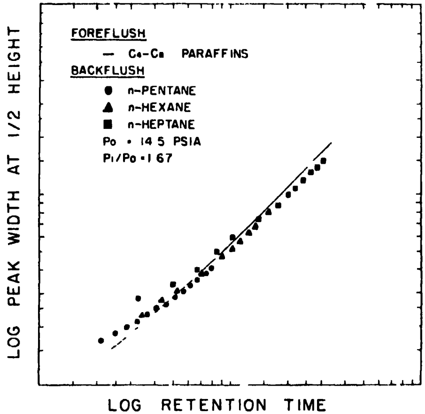

Fig 5 Peak widths of backflushed and foreflushed paraffins

5 % and 10 % as the difference in retention times is increased to 0.27 and 0 39 widths, respectively. To achieve a desired level of accuracy, it is necessary only that the retention times be grouped within a specified interval of time.

With calibration procedures utilizing mixtures of known composition, the requirements are probably less exacting, particularly where the distribution of the heavy components does not depart radically from that of the calibration blend over the expected range of composition. It is necessary

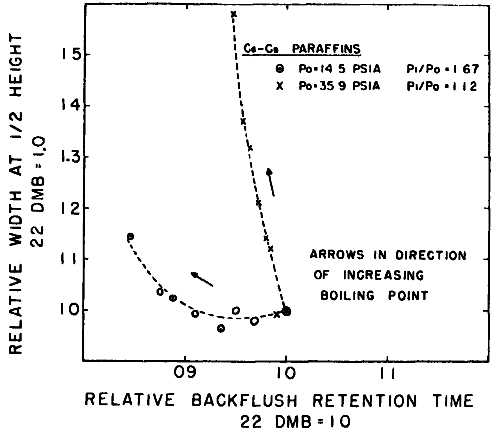

FIG 6 Effect of column outlet pressure on peak width

that these factors be taken into account in order to determine the grouping which will be required for a given application. For the purposes of this discussion, the effect of calibration on accuracy will not be considered.

One can conclude from Fig. 1 that the difference in retention times of backflushed components can be minimized by operating the column at a ratio of inlet to outlet pressures as close to unity as practicable. To this end, it would be desirable to minimize the length of the column and to use low carrier gas flow rates. From the standpoint of the effect of the carrier gas viscosity on the pressure drop, it would be advantageous to use hydrogen at as low a temperature as possible.

Since for the majority of applications the column parameters are to a great extent determined by the analysis which is required in the foreflush mode, the means of achieving the desired grouping may be limited as to choice. If all that is required of a column is that it separate the lighter boiling components from those to be backflushed, it may be possible to achieve the required grouping simply by using a short column at a low carrier gas flow. The analysis of a sample of technical grade propylene for total C_4 content by this means is shown in Fig. 7.

The backflush retention times were determined individually only for isobutane and *cis*-butene-2 using separate 1% samples in hydrogen. These represent the extremes in retention times for the common C_4 paraffins and olefins. A comparison of the observed and theoretical backflush retention times for these two isomers is given in Table I.

What is more significant than the slight discrepancy between the theoret-

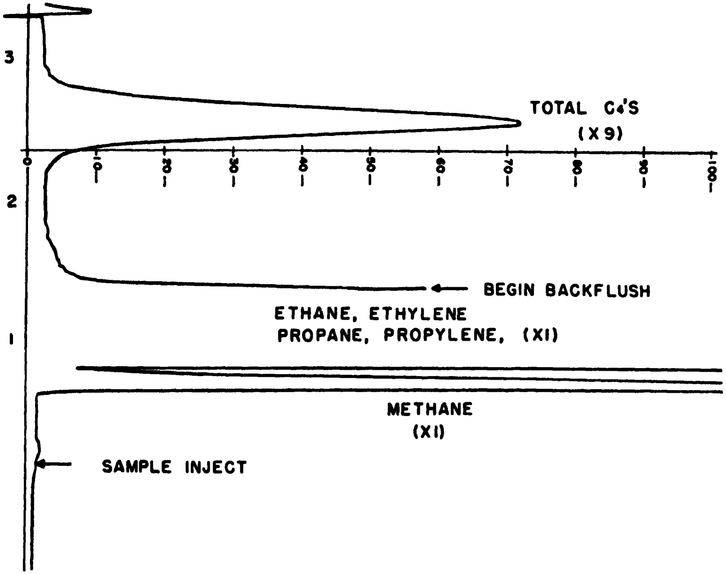

FIG 7 Backflush analysis of total C_4's in propylene. Instrument: Beckman 120-A Industrial Gas Chromatograph; column · 5 ft; packing: 30% silicone oil on 42–60 mesh C-22; hydrogen carrier gas: 38 ml/min; temperature: 50°C, P_i = 1 3 psig: P_i/P_o = 1 09; attenuation as indicated

ical and observed retention times is the good agreement between the differences in retention times of the two components, since it is this difference that is of real concern. When a sample containing 1 % of each of the two components was backflushed under identical conditions, the observed backflush peak height was 98 % of the sum of the calculated individual peak heights. This is the order of error which would be expected on the basis of the observed peak widths (0.20 min) and difference in backflush retention times.

In those applications requiring more complete separation of the foreflush components, it is necessary to use columns longer than that described above. It is then impractical to obtain the required P_i/P_o ratio simply by maintaining a low inlet pressure because of the unnecessarily long retention times concomitant with the resulting low flow rates. In those instances, it may be advantageous to operate the column at an elevated outlet pressure, as was described previously, particularly if the backflushed components do not differ greatly in boiling point or molecular weight.

TABLE I

BACKFLUSH RETENTION TIMES OF C_4'S

Component	Backflush retention time, min	
	Observed	Theoretical
Isobutane	2.64	2.682
cis-Butene-2	2.61	2.657
Difference	0.03	0.025

NOTE. Instrument: Beckman 120-A Industrial Gas Chromatograph; column: 5 ft; packing: 30% silicone oil on 42–60 mesh C-22; hydrogen carrier gas: 38 cc/min; temperature: 50°C; backflush time (t_f) = 1.35 min; P_i = 15.8 psia; P_o = 14.5 psia; P_i/P_o = 1.09.

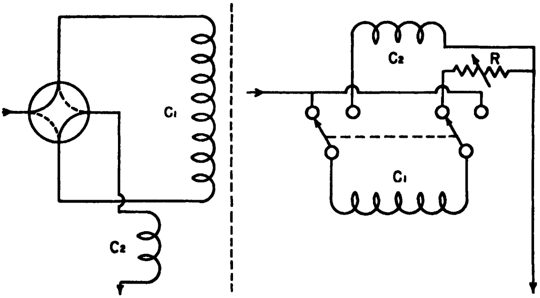

FIG. 8 Valve arrangement for backflushing through regrouping column. Left: Beckman GC-2 Gas Chromatograph Right. Beckman 120-A Industrial Gas Chromatograph C1: main column, C2 regrouping column; R variable restrictor.

In those cases wherein the required grouping is not practical using the above techniques, the use of an auxiliary, or "regrouping" column may be necessary. The arrangement is such that the backflush components, upon emerging from the main column, are diverted into the regrouping column and undergo the normal separation process. The valving arrangement used in the laboratory and industrial instruments is schematically illustrated in Fig. 8. Since the order of backflush elution is the reverse of that in foreflush, (with the heavier components emerging first) the length of the regrouping column can be so selected that it just exactly compensates for the separation between any two peaks in the backflushed group. It should be noted that the relative differences in backflush retention times are such that it is impossible to precisely regroup more than two components.

The backflush retention times of the C_6–C_8 paraffins with and without the regrouping column are compared in Table II.

TABLE II

Backflush Retention Times of C_6–C_8 Paraffins

Component	Backflush retention time, min	
	Without regrouping column	With regrouping column
2,2-Dimethylbutane (22 DMB)	10 28	10.63
2,3-Dimethylbutane (23 DMB)	9.95	10.37
3-Methylpentane (3 MP)	9.78	10.25
n-Hexane	9.62	10.15
2,4-Dimethylpentane (24 DMP)	9.36	10.08
2,3-Dimethylpentane (23 DMP)	9.13	10.00
n-Heptane	9.00	10.05
n-Octane	8.71	10.63
Range	1.57	0.63

Note: Instrument: Beckman GC-2 Gas Chromatograph; main column: 12 ft; regrouping column: 9 inches; packing: 30% silicone oil on 42–60 mesh C-22; helium carrier gas. 55 ml/min; temperature: 77°C; P_i = 25 2 psia; P_o = 14 5 psia; P_i/P_o = 1.67.

In this instance, the length of the regrouping column was chosen to exactly regroup 2,2-dimethylbutane (22 DMB) and *n*-octane. Any other pair of components could have been regrouped exactly by using different lengths. The length required can be closely calculated from the foreflush retention volumes, although some adjustment may be required after one or two preliminary runs, as was the case in our experimental work.

Figure 9 shows the analysis of a paraffinic sample consisting primarily of C_4's and containing a few per cent of material heavier than C_4. The regrouping column in the illustrated case was designed for the backflush measurement of isopentane, *n*-pentane, and 22 DMB. The observed backflush retention times for these components are given in Table III.

The width at half-height of the backflush components was on the order of 0.4 minutes, the 22 DMB peak being somewhat wider than either of the pentanes.

It should be emphasized, at this point, that in peak height measurements the "effective" detector response is a function not only of the detector response as described by Messner, Rosie, and Argabright (*5*), but also of the relative width of the peak. Among isomers of a given carbon number, the differences in detector response as well as in backflushed peak widths are small compared to the differences among carbon numbers. It is obvious that the sources of error are increased by grouping compounds of different carbon number. In any analytical procedure embodying such a measurement, the "effective" detector response must be considered before the limits of accuracy can be established.

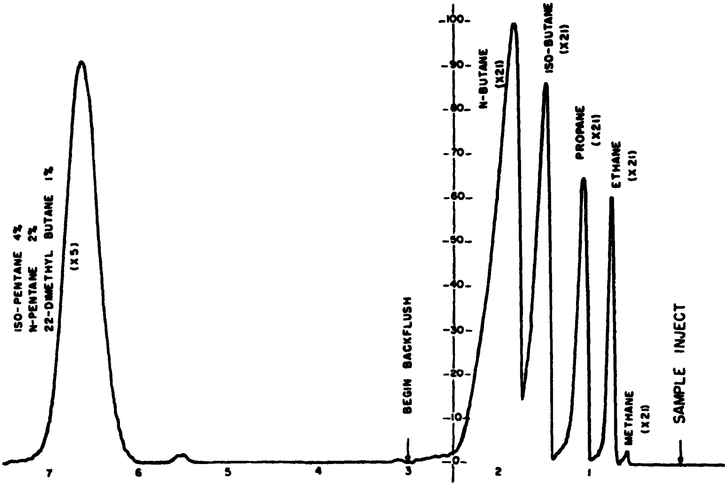

Fig 9 Use of regrouping column in backflush analysis of C_5+. Instrument: Beckman 120-A Industrial Gas Chromatograph; main column: 8 ft; regrouping column: 11 inch; packing: 30% silicone oil on 42–60 mesh C-22; hydrogen carrier gas: 54 ml/min; temperature. 50°C; $P_i = 3.0$ psig; $P_i/P_o = 1\ 21$; attenuation as indicated.

TABLE III

Backflush Retention Times of Heavier than C_4 Material

Component	Backflush retention time, min
Isopentane	6.66
n-Pentane	6.64
22 DMB	6.71
Range	0 07

Note: Instrument: Beckman 120-A Industrial Gas Chromatograph; main column: 8 ft; regrouping column: 11 inches; packing. 30% silicone oil on 42–60 mesh C-22; hydrogen carrier gas: 54 cc/min; backflush time (t_f) = 3 0 min; $P_i = 3.0$ psig; $P_i/P_o = 1.21$.

The maximum difference in backflush retention time which can be tolerated for a given level of accuracy can be increased by the use of substrates which give wider peaks. The analysis of two natural gas samples, with a backflush measurement of C_4's and heavier, over a heavily modified silica gel is shown in Fig. 10. The width at half-height of the individual backflushed components is tabulated in Table IV. The difference in retention

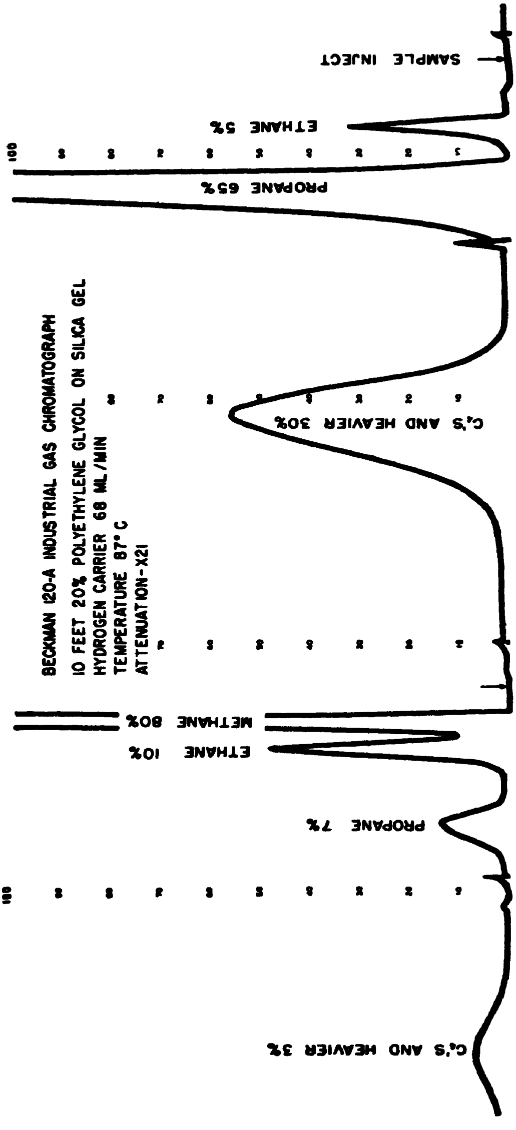

FIG 10 Backflush analysis of C_4+ in typical natural gas plant samples Instrument: Beckman 120-A Industrial Gas Chromatograph; column: 10 ft; packing: 20% polyethylene glycol on silica gel; hydrogen carrier gas: 68 ml/min; temperature: 87°C; attenuation: × 21.

TABLE IV

Half-Height Widths and Detector Responses of Backflushed Components

Component	Backflush retention time, min	Width at half-height, min	Relative width at half-height	Relative detector response
Isobutane	8.92	1.85	1.05	0.96
n-Butane	8.85	1.76	1.00	1.00
Isopentane	8.73	2.28	1.29	—
n-Pentane	8.72	2.14	1.29	1.24
22 DMB	8.70	3.22	1.83	1.37
23 DMB	8.67	3.21	1.82	1.37
3 MP	8.67	3.10	1.76	1.40
n-Hexane	8.63	2.80	1.59	1.45
24 DMP	8.67	4.00	2.27	1.52
23 DMP	8.50	4.27	2.43	1.59
n-Heptane	8.57	4.00	2.27	1.68
n-Octane	8.55	5.19	2.93	1.88
Range	0.37			

Note: Instrument: Beckman GC-2 Gas Chromatograph; column: 4 ft, packing: 20% polyethylene glycol on 35-60 mesh silica gel; hydrogen carrier gas: 40 ml/min; temperature 77°C; sample size. 0.001 ml liquid, 0.20 ml gas, backflush time (t_f) = 4.50 min; P_i = 1.85 psig

times between isobutane and *n*-octane is on the order of only 0.2 times the width of the narrowest peak.

A rather fortunate characteristic of this column material is that the increase in peak width compensates for the increase in detector response. The relative responses, as given by Messner *et al.*, have been normalized to *n*-butane and are tabulated in Table IV for comparison.

Summary

The differences in retention times of backflushed components can be explained on the basis of the pressure gradients which exist in a chromatographic column, and are expressly related to the ratio of inlet to outlet pressures, the foreflush retention times of the components, and the time at which backflushing is begun. These differences in backflush retention times will introduce additional error into analytical procedures which embody measurements based on peak height, rather than area. Several means of minimizing these differences by manipulation of operating parameters are possible. In general, the conditions which favor closer grouping of components are: (1) short columns; (2) low resistance to flow; (3) low carrier flow rates; (4) ratio of inlet to outlet pressure near unity; and (5) wide peaks.

By implication, it would then be advantageous to use hydrogen as the carrier gas, low temperatures, and elevated outlet pressures. Furthermore, the inert support should have large particle diameter. The choice is in most cases dictated, or at best restricted, by the required analysis in the foreflush mode.

A more generally applicable technique embodies the use of an auxiliary column downstream of the main column in the backflush mode to regroup the components. While this technique appears to be able to bring only two components into coincidence, the remainder are closely grouped. Regrouping components of different molecular weight introduces other errors related to differences in detector response and peak width; hence, where the highest accuracy is required, it may be practical to group only isomers of a given carbon number (and, hence, a narrow boiling range); a situation in which this latter technique might prove superior.

The use of columns which provide relatively wide peaks can, in some instances, eliminate the necessity for precise regrouping. A column of this type used in this work has the further advantage of compensating to some degree for the differences in detector response, thus making the measurement of mixed molecular weights more practical.

Some observations regarding the width of backflushed peaks were made incidental to the main work. Peak width was found to be primarily dependent on the absolute retention time of the peak, but appeared to be influenced by the molecular weight as well. This latter effect was more pronounced at the elevated column outlet pressures.

ACKNOWLEDGMENT

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CHAPTER VI

A High-Vacuum Ionization Detector for Gas Chromatographic Analysis

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INTRODUCTION

A high-vacuum ionization gage detector was reported by Ryce and Bryce (*9*) in 1957. In this paper the authors elaborated on the design and sensitivity of the detector, but did not supply data on detector performance under actual analysis conditions. The present work was undertaken primarily to evaluate a high vacuum ionization gage detector under actual analysis conditions and secondarily to improve the detector sensitivity and response characteristics by modifying certain design and operational aspects reported by Ryce and Bryce.

SUMMARY

An all metal, high-vacuum ionization gage detector suitable for analytical gas chromatography has been designed and constructed in this laboratory. The apparatus can be used in conjunction with conventional or capillary columns to detect sample components at the part per million or percentage concentration level. Although lower detection limits can be obtained, the detector is operated so that 0.25 ppm of a C_1–C_4 hydrocarbon (10^{-11}–10^{-13} mole) can be detected in a 5.0-cc sample charge. Larger (10–25 cc at 760 mm) sample charges have been used successfully with the detector.

THEORY AND DESIGN

As has already been noted by Ryce and Bryce (*9*) many of the detectors in use today possess an inherent sensitivity limit in that they must sense a very small change caused by the material which is eluted in some physical or electrical property of the total gas stream. In short, these detectors must measure a small difference between two large quantities. Differential detectors such as the glow discharge (*4*, *8*) gas density balance (*5*), and thermal conductivity cell are examples of this type.

If, however, the detector can be made to respond only to the eluted material and not to carrier gas, a hundred- or thousandfold increase in sensitivity can be realized (*9*). Detectors of this type include the β-ray ionization (*6*) and the high-vacuum ionization gages (*9*).

A high-vacuum ionization gage is potentially a very sensitive and versatile detector. In such a detector the ionizing energy of the thermally emitted electrons can be adjusted to a value which causes ionization of all or part of the eluted materials without ionizing the carrier gas. If care is taken to operate the detector at pressures corresponding to molecular flow, there is the possibility of obtaining linear response from sample components which vary from the parts per million to the 100% concentration level.

Helium has the highest known first ionization potential (24.46 ev) (*9*) and, consequently, it is with helium carrier gas that the maximum sensitivity of the high-vacuum ionization detector can be realized. In the apparatus described by Ryce and Bryce the energy of the ionizing electrons could not be raised above 18.0 ev without ionizing helium. The authors attributed this fact to the Maxwellian energy spread of the electrons leaving the filament. Admittedly the electrons leave the filament with a Maxwellian energy distribution, but less than 1% have energies greater than one electron volt (*7*). The potential drop across the filament, not the Maxwellian energy spread, supplied the added 6.5 ev required for ionization of helium. The RCA 1949 ionization gage used by Ryce and Bryce employs a tungsten filament operated at 5.0 volts AC, equivalent to a peak potential of 7.0 volts. This added to the 18-volt accelerating voltage, for a total of 25 volts, is sufficient to ionize helium.

The potential drop across the filament can be reduced by increasing filament diameter and/or shortening the filament length. The energy spread of the ionizing electrons can be reduced if a collimating aperture limits the number of emitted electrons which enter the ionizing region. This energy spread can be further reduced if the filament is heated with direct rather than alternating current. Electrons accelerated from a DC-operated filament do not contain those high and low energy electrons which arise from the changing amplitude and polarity of applied voltage in AC-operated filaments. We have incorporated a short, DC-operated filament and a collimating aperture in the design of our apparatus and have been able to increase the ionizing energy of the electrons to 23.5 ev without ionizing helium. The collimating aperture ($^{11}/_{64} \times {}^{5}/_{64}$ inch) reduced the energy spread of emitted electrons from approximately 1.55 to 0.43 volts.

Ryce and Bryce evaluated the sensitivity of their detector at a pressure of 700 μ and operated the detector over a pressure range of 20–1500 μ. The mean free path of nitrogen at a pressure of 700 μ is approximately 0.02 cm. It would be physically impossible to fabricate an apparatus in which secondary processes did not occur at a pressure of 700 μ. If the detector is expected to respond linearly to widely varying sample concentrations, it is essential to minimize the occurrence of secondary processes. This can be accomplished by operating the detector at pressures which correspond to molecular flow. To this end, the detector described was operated at pressures of 2 μ or less (the mean free path of nitrogen at a pressure of 1 μ is approximately 15 cm). At these pressures it was found that the detector would respond linearly to a hydrocarbon to at least the 10,000 ppm concentration range, based on actual hydrocarbon concentration in the sample volume (5.0 cc at 760 mm Hg) which was charged to the chromatographic column. With proper signal attenuation there is no reason to believe that the detector will not respond linearly to sample concentrations over the 0.0025–95.0+ % concentration range. This aspect of detector performance is now being investigated.

The signal-to-noise ratio and reproducibility of the high-vacuum ionization gage detector is adversely affected by very small fluctuations in filament emission, electron energy, and pressure. The summed stabilities of these parameters determine the over-all stability and hence the sensitivity and detection limit of the detector. In the present apparatus, for example, the baseline noise is ½ chart division (1.0 mv) which corresponds to an over-all detector stability of 1 part in 1000 or 0.1 % regulation. Consequently, filament emission, electron accelerating voltage and detector pressure must each be regulated to better than 0.1 %. It was found, however, that the detector output signal was ten times more sensitive to a change in electron accelerating voltage than an equal change in filament emission. It follows then that the electron accelerating voltage must be regulated to better than 0.01 %. A change of 5×10^{-7} mm Hg in pressure outside the ionizing region of the detector was equivalent to 0.1 % regulation of pressure. It was found that the total detector background was equivalent to a sample charge containing 150 ppm of a C_2–C_4 hydrocarbon. Closer examination revealed that 120 ppm of this background came from carrier gas impurities while 30 ppm came from back streaming of diffusion pump vapors.

The potential difference (ca. 25 volts) between the filament and the electron accelerating grid is small enough to permit the formation of a space charge (*1*) near the filament unless the electron accelerating grid is placed very near the filament. If a space charge does develop near the filament, the emission regulator will not function properly and will often allow the filament to burn out. The filament and electron accelerating grid of the detector described in this paper are separated by a distance of 1 mm. It was found that space charge effects appeared if this distance was increased to more than 5 mm.

APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. The detector housing was a flanged, cylindrical copper tube with an ID of 3¾ inches and a length of 13 inches. Located in the housing were two corrugated copper baffles and the detector electrode assembly. Vacuum tight joints on each end of the housing were made by means of "O" rings and flanges. Attached to the top flange of the detector housing were thermocouple and ionization vacuum gages, a metering valve and a male octal socket. Flanged directly to the bottom of the detector housing was an oil diffusion pump.

The detector electrode assembly finally developed is shown in Fig. 2. With the exception of the filament leads the entire assembly was fabricated from Nichrome V material; filament leads were 0.040-inch nickel-coated copper. The filament was a 1 cm length of 0.0069-inch rhenium wire. The ionizing region of the detector was enclosed by a 1 × 1 × 5 cm rectangular box; the electron accelerating electrode formed three sides and the ends of this box while the collector electrode formed the top of the box. Thin strips of mica were used to insulate the collector electrode from the electron accelerating electrode. Effluent gas from the column entered the ionizing region through a 3 × 8 × 75 mm channel and escaped into the detector housing by passing through very small slits in the rectangular box. In this manner it was possible to maintain a differential pumping rate across the ionizing region into the detector housing. It was found that a differential

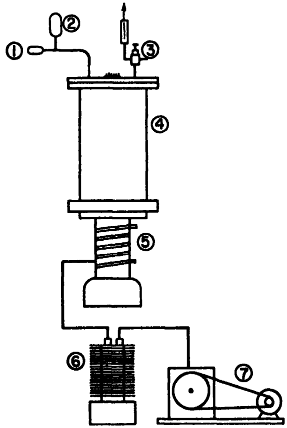

Fig 1. Schematic diagram of apparatus. (1) Thermocouple gage; (2) Model 507 ionization gage; (3) Ideal No. 54-2-12 needle valve; (4) ionization gage housing; (5) MCF-60 oil pump; (6) VMF-20 oil pump; (7) Welch 1402-B pump.

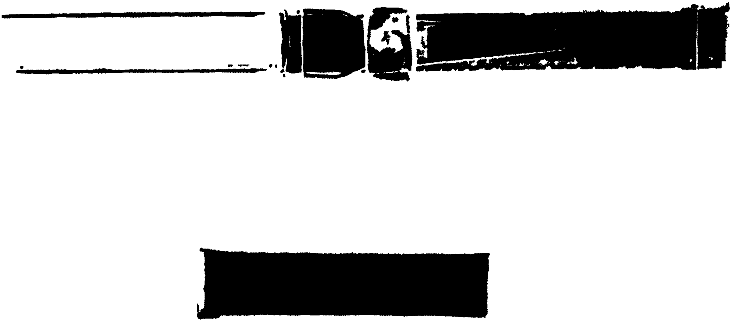

FIG. 2. Electrode assembly.

pumping rate across the ionizing region was a major aid in obtaining a high signal to noise ratio from the detector.

A type 501 (National Research Corporation) thermocouple gage was used to indicate detector pressures down to 5 μ; a type 507 (National Research Corporation) ionization gage was used to indicate detector pressures between 5 μ and 1×10^{-6} mm Hg. The detector was considered vacuum tight when it could be evacuated to a pressure of 2×10^{-6} mm Hg or less. Detector pressures reported here are those measured by the ionization gage in the detector housing. Pressures in the ionizing region were calculated to 5 to 10 times that indicated by the ionization gage.

A stainless steel metering valve (Ideal-Aerosmith, Inc. No. 54-2-12) was used to control the rate of sample admission and therefore the pressure in the detector. In order to ensure rapid detector response to eluted materials the body of this valve was drilled so that the column effluent continually swept through it. The exit end of the chromatographic column was attached directly to the body of the metering valve.

The detector vacuum system included MCF-60 and VMF-20 (Consolidated Vacuum Corporation) oil diffusion pumps in series and a large capacity mechanical pump (Welch Duo-Seal 1402-B). The VMF-20 oil diffusion pump was inserted ahead of the mechanical pump in order to increase the efficiency of the MCF-60 oil diffusion pump. This additional oil diffusion pump greatly improved the over-all stability and pumping speed of the vacuum system for helium. Cold traps in the vacuum system were avoided by the use of corrugated copper baffles. These baffles were located in the

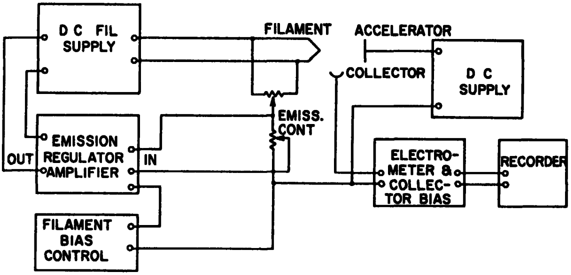

Fig 3 Block diagram of detector electronics

detector housing directly above the throat of the MCF-60 diffusion pump. Each baffle was 2 inches thick and fitted snugly against the detector housing walls by spring action. These baffles did not limit the speed of the vacuum system as used and were quite effective in reducing the amount of diffusion pump vapors in the ionizing region of the detector.

A block diagram of the detector electronics is shown in Fig. 3. The electrometer amplifier and emission regulator were conventional in design and operation. A 100-meg grid resistor was used in the electrometer amplifier. The heating current for the filament was supplied to the emission regulator by a well-filtered DC power supply (Electro Products Laboratories model D-612T). The amplified detector signal could be attenuated in steps which corresponded to 10, 50, 200, 1000, 4000, and 20,000 mv full-scale deflection of a 10-mv strip chart recorder (Leeds and Northrup Speedomax G).

Experimental Results

A 15 ft × ¼ inch column packed with 30% di-*n*-decyl phthalate on Chromosorb W was used to obtain all results reported in this communication The column was operated at ambient temperature with a helium flow rate of 70 cc/min. Helium carrier gas was used directly from the cylinder without further purification. A Perkin-Elmer gas valve with a 5.0-cc sample loop was used for sample introduction.

Using the detector sensitivity parameter S introduced by Dimbat, Porter and Stross (*2*), Ryce and Bryce report a value of S = 312 (*10*) ml mv/mg for a thermistor type detector and a value of S = 30,500 (*9*) ml mv/mg for a high-vacuum ionization gage detector. The value of S obtained for ethene, propene, and *n*-butane with the detector described in this communication was 6,300,000 ml mv/mg, 4,450,000 ml mv/mg, and 5, 250,000 ml mv/mg, respectively. These sensitivities were obtained with the following detector conditions: filament emission = 600 μa, ionizing energy = 23.5 ev, collector voltage = −28 volts with respect to the ionizing region and gage pressure = 1.0 μ. The detection limit of the apparatus under these conditions was ½ chart division (1.0 mv) which corresponded to 0.25 ppm of a C_1–C_4 hydrocarbon. The detection limit corresponds to 8.2×10^{-11} mole of ethylene in a 5.0-ml sample volume and assumes that the entire sample charge passes through the detector. Actually, much less than 1% of the sample charge passes through the detector. It should be pointed out that the sensitivities listed above are not the ultimate that could be obtained; higher sensitivities can be obtained by increasing sample volume or detector pressure. Additional sensitivity could also be achieved by reducing substrate vapor pressure and carrier gas impurities.

Figure 4 shows the variation of detector response to several hydrocarbons as a function of electron ionizing energy. The nonlinearity of these plots is characteristic of polyatomic ionization efficiency curves. The detector re-

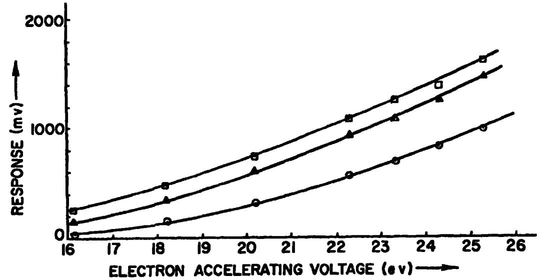

Fig. 4. Detector response vs. accelerating voltage. ⊙, methane; △, *n*-butane ◻, propene; sample volume: 5 0 cc; filament emission: 980 μa; detector pressure: 1 0 × 10^{-3} mm Hg.

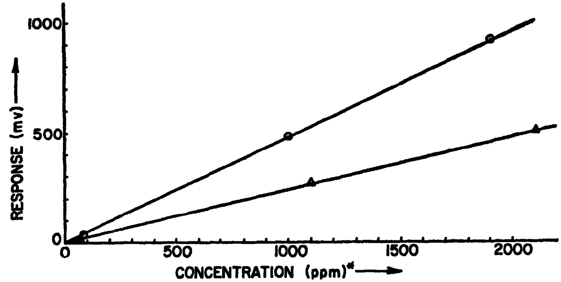

Fig 5. Detector response to hydrocarbon vapors. ⊙, *n*-butane; △, methane; sample volume: 5.0 cc; accelerating voltage: 22.0 ev; filament emission: 980 μa; detector pressure: 1 0 × 10^{-3} mm Hg.

* Mole concentration in sample charge

sponse to various hydrocarbons as a function of concentration is shown in Fig. 5. As expected, this plot is linear. A study of detector response to various compounds above the 1 % concentration level is in progress.

The chromatogram of a sample containing ethene (35 ppm), propene (50 ppm), and *n*-butane (50 ppm) is shown in Fig. 6. It was found that unsymmetrical elution curves and slow detector response were generally the result of dead volume in the metering valve.

Discussion

At an early stage in the development of the present detector, a beam-forming device was investigated in the hope of increasing detector sensitivity. This device was designed to form a circular, 0.005-inch beam of molecules in the ionizing region of a detector similar to a conventional ionization gage. The resultant increase (10-15 %) in sensitivity did not warrant its inclusion in the design of the detector. Another scheme for improving sensitivity was the application of a weak magnetic field to collimate or increase the number of electrons in the ionizing region of the detector. The approximately 25 % increase in sensitivity realized was not

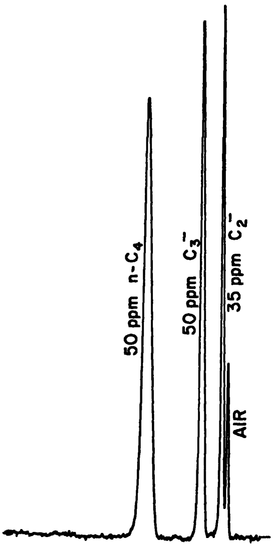

Fig 6. Chromatogram of synthetic mixture Electron energy: 22 1 ev; detector pressure: 1 25 × 10^{-3} mm Hg; filament emission: 980 μa, sample volume: 5 0 cc, helium carrier.

considered worth the added complexity. The use of differential pumping across the ionizing region was much more effective in increasing sensitivity and signal-to-noise ratio than the combined effect of a magnetic field and molecular beam.

Both rhenium and tungsten filaments were evaluated for detector use. At operating pressures of 1 μ or higher, the rhenium filament was much superior to the tungsten with respect to surface oxidation and carbonization. The rhenium filament, however, did show a greater tendency to warp than the tungsten. Results to date indicate that greater detector stability and reproducibility can be obtained with a rhenium filament.

Several systems were evaluated for metering column effluent into the detector. These systems included porous plugs, capillary tubing, a VEECO type VL variable leak, a HOKE type 2RB285 needle valve, and an IDEAL type 54-2-12 metering valve. Adequate control of detector pressure could be maintained with either the IDEAL or HOKE metering valves. The IDEAL metering valve, because of its smaller internal volume, was used in preference to the HOKE valve.

CONCLUSIONS

An extremely sensitive and versatile gas chromatographic detector system has been constructed in this laboratory. Both capillary and conventional chromatographic columns can be used with the detector. The detector requires the order of 0.5 cc atm/min of sample. The detector can be used for the analysis of sample components in the percentage or part per million concentration range and does not give nonlinear response or "saturate" when 1.0–10.0-cc sample volumes are used. The detector is virtually independent of column temperature or carrier gas flow rate and can be used to detect any material which can be vaporized in the carrier gas stream.

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CHAPTER VII

A Radio Frequency Discharge Detector for Gas Chromatography

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The design of a more sensitive detector for gas chromatography was undertaken in the hope that the use of smaller samples would result in an increase in the resolving power of chromatographic columns. Among possible detection methods, those which depended on a change in the electrical properties of the carrier gas seemed to promise greatest sensitivity, and several of these methods were investigated.

In the detector described by Harley and Pretorius (*1*) a change in conductivity of an electric discharge excited by direct current at low gas pressure indicated the passage of an organic vapor through the discharge. In our experiments, we noted considerable instability of this discharge, apparently caused by sputtering from the cathode surface, and by the deposition of carbonaceous material on the cathode surface following passage of an organic vapor. Direct current discharges excited in helium at atmospheric pressure between pointed electrodes were subject to similar causes of instability. The electrode configuration found to give greatest stability for this latter mode of operation was the somewhat impractical combination of a metal anode and a concentrated sulfuric acid cathode. The sulfuric acid, apparently because of its reactivity with impinging fragments of organic vapors, was less subject to surface change by carbon deposition.

In the direct current electric discharge detector, instability was attributed to the important part played by the electrode material and the electrode surface in maintaining the discharge. The feasibility of maintaining a stable discharge at radio frequencies has been demonstrated by Lion (*2*) in the construction of a sensitive mechanic electric transducer. It was felt that the use of radio frequency (RF) voltages to excite the discharge would overcome the instability because of the lesser part played by the electrode material and surface.

By the use of radio frequency voltages, it was found possible to excite a stable glow discharge in flowing helium at atmospheric pressure. The sensitivity of this discharge to changes in the composition of the gas has permitted the construction of a gas chromatography detector of high sensitivity.

EXPERIMENTAL

The use of radio frequency discharges permits variety in the geometry of the detector cell as well as in the method of monitoring analyses. The method of operation to be described is one that was designed for use with packed chromatographic columns chosen for its simplicity of operation.

The electrode configuration found most convenient has been a wire, 0.020 in. OD, 1 in. long, mounted along the axis of a cylinder from $\frac{1}{8}$ to $\frac{3}{16}$ in. in diameter. RF power was supplied from a crystal oscillator and power amplifier, (RCA tube 6146), supplied with a constant high voltage from a regulated power supply. Because of the desirability of maintaining the detector at temperatures higher than that of the column to prevent condensation of the vapor within the detector, the power is conducted to the central wire by a coaxial cable followed by a Tesla-type, tuned, step-up RF transformer. The transformer and attached central wire are matched to the transmitter by a conventional pi-section antenna matching network. For more complete temperature isolation of the detector cell, the Tesla transformer was located in the temperature-controlled bath with the detector cell.

The materials used for the central wire have included stainless steel, tungsten, and platinum, with little difference in behavior noted. Cylinders have been made of either brass or stainless steel for ease in construction.

Using this geometry, a discharge excited in flowing commercial helium is self-starting at low RF voltages. The discharge surrounds and is limited to the vicinity of the central wire, and appears to be uniformly distributed in intensity along its length. With progressive increase in RF power supplied to the wire the discharge first uniformly increases in diameter and intensity and then breaks down into an erratic, localized arc of higher intensity. The RF power is adjusted to the range producing uniform glow. The amount of power that can be supplied to the discharge without producing an arc increases with increase of the frequency of the voltage used. We have tested frequencies ranging from 5 to 40 Mc. At higher frequencies, the increasing significance of the stray capacitance of the connections to the electrodes makes the construction of electrodes more critical. Twenty-seven megacycles was chosen as a compromise optimum frequency.

The addition of gases other than helium to the glowing helium discharge causes a diminution in the diameter of the glow, a change in its color dependent upon the kind of vapor added, and a host of changes in its electrical characteristics. The occurrence of a glow discharge "loads" the RF circuit, causing a decrease in the RF voltage across the tuned transformer. There is an increase in the RF voltage when the discharge is reduced in intensity, probably as a result of decreasing the "loading" of the circuit. There is a shift in the resonant frequency of the circuit of which the detector cell is part, best observable with RF sources lacking frequency control, presumably explainable, at least partly, by the change in capacitance of the discharge tube secondary to the change in size of the glow. There is a decrease in the direct current electrical conductivity between the wire and the cylinder wall, also possibly secondary to the change in size of the glow.

The excitation of a glow discharge in a nonuniform alternating current field results in direct current potential gradient across the field. The rectifying action of the helium discharge provides a most convenient parameter to monitor the discharge, and thus to indicate the passage of vapors through the detector. Under usual operating conditions, the central wire is approximately 50–60 volts negative with respect to the cylinder, and acts as a source of from 50 to 100 μa of direct current with an internal resistance of from 0.5 to 1 meg. The internal resistance of the cell is a function of the cylinder diameter. In the range of power and glow diameter used, the internal resistance increases markedly when the cylinder diameter exceeds ¼ inch. The direct current is measurable between the central wire and the cylinder wall in the presence of higher radio frequency currents through the same conductors by means of simple electrical filters. The voltage drop across a small resistance connecting the central wire and the cylinder wall can be applied directly to a millivolt recorder without preamplification.

Passage of an organic vapor through the discharge causes a decrease in the direct current from the discharge tube. The direct current drops to zero as the discharge is extinguished by larger concentrations of vapor. The discharge starts spontaneously as the concentration of vapor decreases and the direct current returns to the original level after the peak passes.

To make the signals appear as positive deflections, the current is balanced by the current from a dry cell of approximately equal voltage passing through a variable resistance. Passage of a vapor through the cell is thus indicated by an unbalanced current of the dry cell. Under usual operating conditions, 500 ohms connects the central wire and the cylinder wall. The voltage across this resistance is divided to provide convenient selection of sensitivity range.

The fractional decrease in the direct current is directly proportional to the concentration of the organic vapor in the helium. Close agreement has been found between the analyses of samples of mixtures done with this detector and the analyses of the same samples done with thermal conductivity detectors (Table I).

The linearity of response with respect to concentration, judged by the shape of the curves, extends to the upper concentration level where the direct current is reduced to approximately 25% of the baseline value.

TABLE I

COMPARATIVE ANALYSES IN PERCENTAGE COMPOSITION OF THE SAME MIXTURE OF METHYL ESTERS USING THE RF DETECTOR AND THE HOT WIRE THERMAL CONDUCTIVITY DETECTOR

Detector	Methyl ester					
	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18}'
RF	0.85	10.0	7 1	30	24	27
TC	1.0	10.7	7.2	28	24	30

SENSITIVITY

The sensitivity of the detector has been studied by the injection of known small quantities of materials, and by connecting the detector cell in tandem with thermal conductivity cells so that simultaneous records could be obtained from the output of both detectors operating on the same samples and concentrations of organic materials.

Small samples of mixtures of methyl esters of fatty acids were analyzed by a 6-ft, ¼-in. diameter column packed with Celite coated with a polyester of succinic acid and diethylene glycol operated at 200°C. The current through a commercial hot wire katharometer was set at 300 ma, and the records were obtained with minimal attenuation of the signal. In order to obtain curves from both detectors, the RF detector was operated in a sensitivity range where full-scale recorder deflection represented a decrease in 25% of the total direct current. Since, in general, the detector operates with no noise when a decrease of 5% of the direct current is represented as full-scale deflection, this analysis was considered to have been run at ⅕ total sensitivity. The results of this analysis are shown in Fig. 1, and from this record and the companion records obtained, the sensitivity ratio was estimated to be approximately 50:1, indicating approximate actual sensitivity ratio of 250:1.

In order to estimate the sensitivity of the detector by the analysis of precisely known small quantities of materials, a sample introduction method was developed for the injection of samples in the microgram range (*3*). Samples were collected in small glass capillaries, diameter 0.05 mm, the small capillary sealed into a slightly larger glass capillary, and the length of the liquid column measured with a measuring microscope, from which the sample volume could be determined. A series of devices were developed for delivery of these capillaries to the heated column inlet without interrupting the flow of carrier gas, and for crushing the capillary at that point, thus injecting the sample. Using 6-ft packed columns, it is possible to do an analysis of a mixture of methyl esters of fatty acids using 1 μg of total

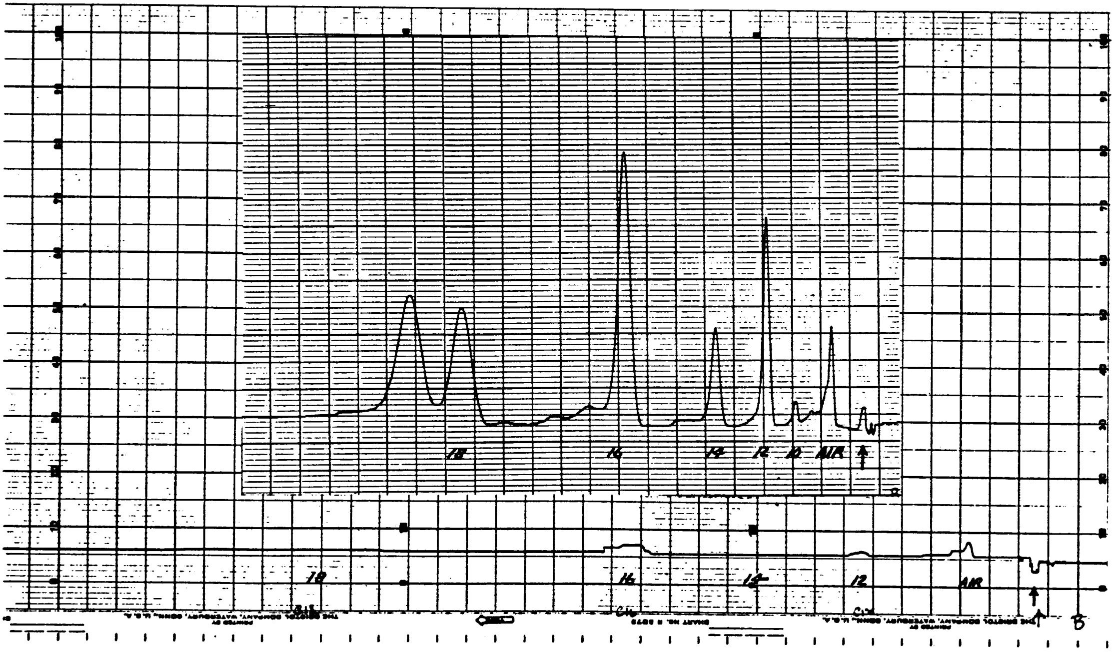

FIG. 1. Record obtained using RF detector, attenuated 5×, superimposed on record obtained simultaneously from same volume effluent, using katharometer at full sensitivity (recorded at different chart speeds). Methyl esters are designated by number of carbon atoms in the fatty acid.

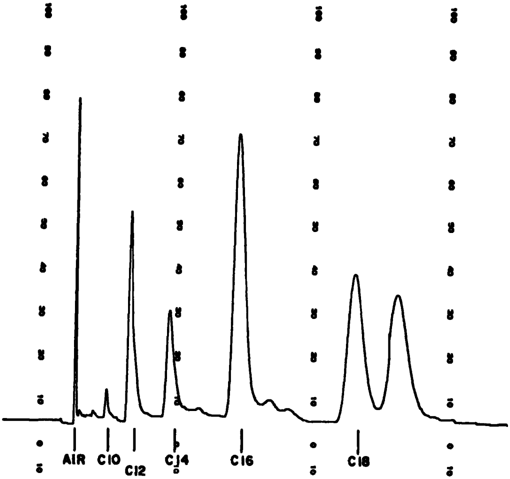

FIG. 2 Analysis of a mixture of methyl esters, designated by a number of carbon atoms of the fatty acid Total sample size 3×10^{-6} grams

sample. The results of an analysis done on 3 µg are shown in Fig. 2. The early peaks represent less than 10^{-8} gm of materials, or approximately 10^{-11} moles. Using a "signal-to-noise ratio of 2:1" to define the lower limit of detectability, this record would indicate a lower limit of 10^{-12} moles for analyses of this type.

The lower limit of sample detectability is dependent on the efficiency of the column. The sensitivity of the detector as calculated from the methyl laurate (C_{12}) curve on the figure is the ability to detect 3 molecules of methyl laurate per 10^9 molecules of helium at twice the noise level.

Although the method of expressing sensitivity as a ratio of number of molecules of vapor to number of molecules of carrier gas is appealing, experiments to determine the response to various organic vapors of different molecular weights indicate that the detector gives a response proportional to the weight of the materials, rather than a response depending on the number of molecules. The compounds tested included higher fatty acid vapors, ethanol, methanol, benzene, methyl butyrate, bromo benzene. The sensitivity in terms of molecular concentration ratio would therefore have to be modified downward when lower molecular weight compounds are considered.

The sensitivity of the detector as described has been found sufficient for use as a detector for capillary columns in which considerably less than 1 μg samples of mixtures of fatty acid esters may be analyzed. In preliminary work done at the time of this writing, the operation of a detector cell of 0.5 cc volume was modified so that the effluent from the capillary column was diluted by an accessory gas flow of 50 ml per minute prior to entering the detector cell. Using this arrangement 0.1 μg samples of mixtures have been analyzed in time periods greater than 1 hour, and sensitivity to less than 10^{-13} moles is demonstrable. The construction of detector cells of smaller volume is expected to result in another order of magnitude of sensitivity increase by reducing the volume of diluting accessory flow necessary.

EFFECT OF TEMPERATURE, PRESSURE, AND GAS FLOW RATE

The RF voltage necessary to maintain a discharge of given intensity decreases with increase in detector cell temperature. At a given voltage the direct current from the discharge increases with temperature with a several fold increase as the temperature is raised from room temperature to 200°C. Increase of pressure within the discharge tube results in a decrease in the direct current output. Increase in the flow rate of helium through the discharge results in a decrease in the direct current output. The effect of flow rate, therefore, may be thought to result from a decrease in temperature of the wire and an increase in gas pressure in the cell. This effect of flow rate is also attributable to the removal of reactive gases from the discharge, as evidenced by an increase in electrical conductivity downstream of the discharge with increase in flow rate.

The response of the detector to changes in temperature has made it advisable to avoid types of temperature control for the detector in which cycling of temperature occurs. In actual operation, the effect of increasing temperature on the volatility of the stationary phase more than counterbalances the direct temperature effect and causes a decrease in direct current to occur when the temperature is increased.

For convenience in recording, the DC output of the detector has been balanced by the use of a dry cell. One can balance the effect of temperature variation in the detector bath by the use of a second or reference detector cell, but since the effect of temperature on volatility of the liquid phase is greater, this would entail use of a reference column as well. A result of the use of a constant balancing system is that changes in the operating conditions of the column that occur during an analysis are displayed on the record. This may result in records sometimes less aesthetically pleasing than those obtainable using methods of detection in which an increase in ion current following passage of an organic vapor is measured. In these other detection methods, the baseline is ideally near zero current and changes in operating conditions introduce variability in sensitivity rather than change in the baseline. We have considered operation of this detector in a similar manner, in which an increase in electrical conductivity downstream from the discharge would indicate the passage of an organic vapor, but have concluded that any improvement thus obtained would be more apparent than real, because of the sacrifice of the ability to recognize significant changes in sensitivity should these occur.

Recovery of methyl esters following passage through the discharge has not been possible using methods of collection satisfactory for the collection of esters when the discharge is turned off. More than 90% of small samples passing through the discharge are apparently destroyed. The sensitivity of the detector and its low volume requirement make the use of a fractional bypassing arrangement feasible when collection of samples is desired.

Helium, despite its high ionization potential, sustains a glow discharge at low voltage. Addition of organic vapor, even in small concentration, causes the discharge to diminish in intensity. A similar discharge can be made to occur in neon with a minimal increase in RF voltage. To excite a discharge in argon, however, requires an initial pulse of higher voltage to start the discharge, which is then maintainable using voltages minimally larger than the voltage used with helium. When an organic vapor is mixed with the argon, the voltage necessary to excite a discharge decreases and the argon mixture behaves like helium. Following initiation of a discharge in argon, addition of low concentrations of organic vapor causes an increase in intensity of the discharge while progressively higher concentrations cause the discharge to be diminished and then extinguished.

The electrical conductivity of the gas downstream from the helium discharge depends on the flow rate of gas through the discharge. The electrical conductivity of the gas away from the highly conductive plasma increases moderately when an organic vapor passes through the discharge, despite a simultaneous diminution in the intensity of the discharge. The electrical conductivity of the gas downstream from an argon discharge is an order of magnitude less than that of the helium discharge, but the increase in conductivity with addition of vapor is more marked downstream from the argon discharge.

It has also been observed that the electrical conductivity downstream from the discharge is increased when organic vapor is added to the gas downstream from the discharge. The possibility of utilizing this property in the design of a detector for capillary columns is being investigated.

DISCUSSION

In Lovelock's (*4*) description of his radioactive ionization chamber detector for gas chromatography, he expressed the belief that the relatively high conductivity he observed with helium was caused by impurities in the helium that could be ionized by the metastable states of helium. He attributed the lesser conductivity of argon under the same conditions to the lower energy of metastable argon, which possess insufficient energy to ionize the impurities present.

Some of the experimental results with the RF detector are explainable by an extension of this hypothesis. Initiation of a glow discharge in helium may occur at relatively low voltage because of the presence of impurities ionizable by the energetic, excited states of helium. Initiation of the glow discharge in argon may be more difficult because of the lower energy of the argon excited states relative to the impurities present, but occur easily when an impurity of low ionization potential is intentionally added.

Helium and neon ions have been found to be more efficient in liberating electrons from the surface of the cathode than the other rare gases (*5*). The higher energy of metastable helium atoms may also make them more efficient in dislodging electrons from the electrode surfaces than excited argon. This property may also contribute to the difference in behavior of the two gases. The significance of ionization of the gas in initiating the discharge may be questionable, especially in light of the observation that the addition of small amounts of organic vapor to the helium discharge partially quenches the discharge and at the same time apparently results in an increase in the number of ions present.

In explaining the mechanism of action of this detector, we have had to be content with descriptive explanations rather than a unique theoretical explanation. Further evaluation of the mechanism awaits more knowledge of the composition of the flowing plasma, such as may be obtained by spectroscopic and mass spectrometer analyses.

SUMMARY

It has been found possible to excite a stable glow discharge in helium at atmospheric pressure by the use of radio frequency voltages. The exquisite sensitivity of this discharge to changes in gas composition has made possible the design of a versatile detector for gas chromatography suitable for use with packed as well as capillary columns. Since a large fraction of the organic vapor molecules enters into the reaction in the discharge, a relatively large signal is produced for a given concentration of vapor, permitting use of standard millivolt recorders without preamplification.

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CHAPTER VIII

The Sensitivity of Detectors for Gas Chromatography

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INTRODUCTION

The desirability of reporting detector performance in some standard way has been emphasized (*4*, *5*) with little progress to date toward the goal of a generally accepted and widely understood usage. The sensitivity of a detector used in gas chromatography is usually estimated by obtaining a chromatogram with a known sample. Calculations are then made on the recorded peak using a formula such as recommended by Johnson and Stross (*8*) and first proposed by Dimbat *et al.* (*6*).

There are two problems connected with this procedure which it is the purpose of this paper to discuss. The first is the nature of the sensitivity expression that is most useful for purposes of description and comparison. The second problem is to define experimental conditions which will validate comparisons between different detectors and comparison of the same detector between different laboratories. The first problem assumes importance because of the need for a standard expression to replace a number of different expressions used in the literature. The second problem is of importance since work in this laboratory indicates that sensitivity numbers can vary widely for the same detector, depending upon such experimental factors as flow rate, dwell time, and dilution of the component used to measure the sensitivity.

The present paper examines the meaning of the term "sensitivity" and extends the ideas of the above-mentioned authors by making explicit the relationship between sensitivity and limit of detection. Furthermore, using the definitions proposed in this paper, data are given on the sensitivity and limit of detection of a number of detectors described in the literature. It is proposed that the limit of detection be used to describe the sensitivity behavior of a detector, since this quantity includes the important factor of noise level of the detector system, while the sensitivity does not. Moreover, the limit of detection corresponds more closely to the actual physical situation in which a detector is used in gas chromatography than does the sensitivity.

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With respect to experimental conditions used in measuring detector sensitivity, it is proposed that these be carefully defined.

While this paper deals with gas chromatography detectors, it is believed that the ideas presented will be useful in other areas of instrumental analysis, where concepts of sensitivity and limit of detection are important.

DEFINITIONS OF SENSITIVITY

Consider a situation, such as in gas chromatography, in which the response of a detector is zero when the quantity to be measured is zero. The sensitivity, S, of a detector is the ratio of the change in response, R, to the corresponding change in the quantity measured, Q. This may be written as follows:

$$S = \Delta R/\Delta Q \tag{1}$$

The sensitivity may thus be measured at different levels of Q, and if the response characteristic is not linear, S will vary with the level of Q.

The limit of detection, Q_0, of a detector, is the least amount of the quantity measured which can be detected with a specified degree of certainty. The uncertainty in the detector system is usually termed noise, i.e., it is the response of the instrumental system to random fluctuations in operating conditions, and will be symbolized, R_n. To detect the quantity to be measured with certainty, the response or signal must be greater than the noise, else the response will be indistinguishable from the noise. A number of workers (*3*, *11*, *16*, *17*) have used a factor of twice the noise level to establish the limit of detection with certainty. This figure will be incorporated in the definition of Q_0. Therefore, the limit of detection, Q_0, is that value of the measured quantity which corresponds to twice the noise, R_n. Substituting these corresponding values into Eq. (1), we obtain:

$$S = \Delta R/\Delta Q = 2R_n/Q_0 \tag{2}$$

Therefore:

$$S \times Q_0 = 2R_n \tag{3}$$

Figure 1 has been drawn to illustrate the meaning and relationship of these concepts. S is a slope; Q_0 is the x coordinate of a point on the instrument response curve which can be specified when the y coordinate is specified. Q_0 is arbitrarily specified at twice the noise level; if the slope is known, then Q_0 may be calculated. Conversely, if Q_0 and the noise level are specified, S may be calculated.

It may be useful at this point to outline briefly the experimental determination of the quantities given in Eq. (3). The determination of S follows from its definition given in Eq. (1), i.e., the change in response is measured for a given change in the quantity measured. Q_0 is difficult to

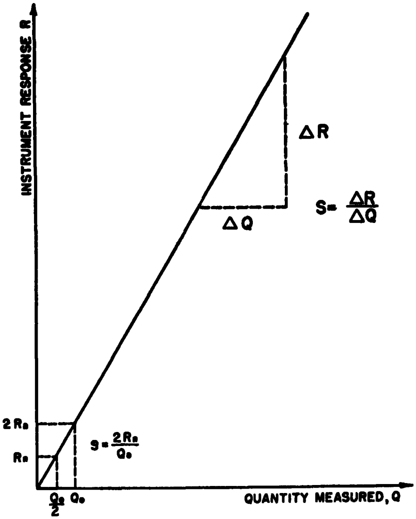

FIG. 1 Instrument response vs quantity measured (relationship between sensitivity and limit of detection)

measure directly and is better calculated through Eq. (3). For this purpose R_n, the noise, must be estimated, and is usually done by taking peak-to-peak values of the noise record. Peak-to-peak estimation involves the drawing of parallel lines through the maximum and minimum points of excursion of the record when no sample is being measured. The measured distance between the lines is then converted to millivolts or microvolts.

The relationships given above are strictly true only if R is a linear function of Q. For large variations of Q this is rarely the case. For small variations of Q, the relationship may be considered as very nearly linear and the above relationships may be employed as useful approximations.

NOISE CONSIDERATIONS

The response of the instrumental system to random fluctuations in operating conditions is considered noise. Such variations in response may be described by a distribution such as observed in the normal curve of error or Gaussian function. If this type of distribution applies, there is a nonzero probability that any arbitrarily chosen peak-to-peak noise value will be exceeded. Thus, there is always some uncertainty in estimating a noise value by the peak-to-peak procedure mentioned above. Hence, there will be some uncertainty in Q_0.

TABLE I

PEAK-TO-PEAK VALUES CORRESPONDING TO VARIOUS RISKS

Probability of exceeding peak-to-peak value	Probability of exceeding peak-to-peak value on one side of trace	Fraction of peaks included in peak-to-peak value	Peak-to-peak value
1 in 1000	1 in 2000	0.999	2 × 3.291 × rms
1 in 100	1 in 200	0 990	2 × 2.576 × rms
5 in 100	5 in 200	0.950	2 × 1.960 × rms

Using a somewhat involved and laborious analysis it is possible to calculate a peak-to-peak noise value the uncertainty of which is as small as one chooses. Williams *et al.* (*18*) have given the procedure for analyzing a noise record, and their paper should be consulted for details. These authors show how to determine the root mean square (rms) value of a noise trace. The rms of a noise record has a definite, non-arbitrary value. With the rms value and a table of the probability integral the analyst can choose peak-to-peak voltage values with as small an uncertainty as he chooses.

Data illustrating this idea have been assembled in Table I, which was drawn up with the aid of the extended tables of the probability integral prepared by the Federal Works Agency (*7*). As Table I shows, the uncertainty or risk in choosing a peak-to-peak value may be expressed in a number of ways: the probability of exceeding a peak-to-peak value, the probability of exceeding a peak-to-peak value on one side of the trace, or the fraction of the total number of peaks included in the peak-to-peak value. The peak-to-peak values are expressed as multiples of the rms value. If it is decided that the peak-to-peak value shall include 99.9% of all the peaks, then the peak-to-peak value is 2 × 3.291 rms. Thus Eq. (3) may be written:

$$S \times Q_0 = 2(2 \times 3.291 \times \text{rms}) = 13.164\ \text{rms} \tag{4}$$

The difference between Eqs. (3) and (4) is that in Eq. (3) one does not know the uncertainty in R_n; in Eq. (4) the uncertainty in R_n is 1 in 1000. If it is known that R_n includes 99.9% of the peaks, then the following identity holds:

$$S \times Q_0 = 2 \times R_{99.9} = 13.164\ \text{rms} \tag{5}$$

One may, of course, choose any other uncertainty that one wishes.

It is of interest to calculate the probability that a peak twice the noise value will be obtained. This has been done in Table II. It can be seen from this table that even if a very poor estimate of the peak-to-peak noise has been made, i.e., one including only 95% of the peaks, the probability of a noise peak twice as high as the peak-to-peak value is very small, and

TABLE II

PROBABILITY OF PEAKS TWICE AS HIGH AS PEAK-TO-PEAK VALUES

Fraction of peaks included in peak-to-peak value	Probability of exceeding twice the peak-to-peak value on one side of the trace	Relative value of Q_0
0.999	Less than 1 in 10^{15}	1.278
0.990	Less than 2 in 10^{11}	1.000
0.950	Less than 3 in 10^{9}	0.762

conversely it is almost certain that a peak this high is signal. Thus, the use of factor 2 in Eqs. (2) and (3) has ample justification. Equation (3) shows that the value of Q_0 will vary with the noise chosen. The third column in Table II has been added to show how the relative value of Q_0 changes, depending on the fraction of the peaks included in the noise value. It can be seen that there is a variation of only 25% around the 99% level. Thus, the experimental procedure for estimating peak-to-peak values described previously leads to only minor variations in the Q_0 value even if R_n is poorly chosen.

The above discussion may be summarized as follows: The peak-to-peak method of estimating noise is very simple experimentally but is attended with some uncertainty, which carries over into an uncertainty in Q_0. The rms method of estimating noise is quite laborious but can give peak-to-peak values with as small an uncertainty as one chooses. Thus, the means for estimating Q_0 with small uncertainty is available. However, the ordinary method of estimating noise, gives Q_0 values whose variation is quite acceptable for purposes of describing detector performance and comparing detectors. If the analyst knows from experience or observation that his peak-to-peak noise value include 99.9% of the noise peaks, then the ordinary procedure will give Q_0 values with very small variation.

SENSITIVITY EXPRESSIONS FOR GAS CHROMATOGRAPHY

The definitions given above for S and Q_0 are consistent with similar definitions given in American Standards Definitions of Electrical Terms (*1*). To translate these general definitions to the case of gas chromatography detectors, we need only specify the units of R and Q. For R, the unit chosen is millivolts, and for Q, the unit chosen is concentration, in units of millimoles per milliliter (mM/ml). The noise level will also be indicated in millivolts and its symbol, as above, will be R_n.

A sensitivity expression has been proposed for gas chromatography by Dimbat *et al.* (*6*). They use the same symbol, S, and their definition follows:

$$S = (A \times C_1 \times C_2 \times C_3)/W \tag{6}$$

where S = the sensitivity, mv ml/mg;
A = the peak area, sq cm;
C_1 = the recorder sensitivity, mv/cm of chart;
C_2 = the reciprocal of the chart speed, min/cm;
C_3 = the flow rate at the column exit, corrected to measuring cell conditions, ml/min;
W = the weight of the component introduced into the column, mg.

This definition is consistent with S as defined in Eq. (1), as can easily be seen if the units of S are written mv/mg/ml. The purpose of writing the definition as in Eq. (6) is twofold: to use the ordinary gas chromatography record to obtain a sensitivity figure; to eliminate from the sensitivity figure the effect of experimental variables such as flow rate or chart speed. Equation (6) may be more simply written as follows:

$$S = (P \times F)/W \tag{7}$$

where P is the peak area in mv min; F is the flow rate in ml/min; and other symbols have the same meaning as before.

A sensitivity expression similar to Q_0 has also been proposed for gas chromatography by Keulemans (*4*). His expression differs from Q_0 only in that the unit for limit of detection is micrograms per milliliter. It would appear to be more useful and meaningful for comparison purposes to use moles or millimoles as the quantity of component, and retain as the unit of volume the milliliter. Introducing, in this way, the need for molecular weight values creates no difficulty because detector calibrations are done with known compounds. In addition, weights or volumes of liquid samples as well as volumes of gaseous samples can easily be converted to moles or millimoles, thus facilitating comparison of detector behavior toward samples in different states.

The use of millimoles to express amount of component rather than milligrams would be justified, furthermore, for thermal conductivity detectors, since the thermal conductivities of common organic vapors are quite similar. For ionization detectors, the ionization potentials of most organic compounds are quite similar (*12*, *15*). On this basis, the sensitivity expressions defined in Eqs. (6) and (7) would be written as follows:

$$S = (A \times C_1 \times C_2 \times C_3)/M = (P \times F)/M \tag{8}$$

where M is the amount of component in millimoles. If Q_0 is calculated from S, as given in Eq. (8), using the appropriate noise figure and Eq. (3), Q_0 will have the units mM/ml as proposed above.

COMPARISON OF SOME DETECTORS

The values in Table III have been assembled to illustrate the usefulness of the above concepts for the purpose of comparison. These values were calculated from data available in the literature and elsewhere. Where sensitivity figures were available on the basis of Eq. (6), the sensitivity was recalculated using the molecular weight of the component, if given; if the component was not indicated a molecular weight of 80 was arbitrarily used to convert from milligrams to millimoles. The values in the column headed pQ_0 were calculated using the relationship:

$$pQ_0 = \log 1/Q_0 \tag{9}$$

EXPERIMENTAL CONDITIONS

Data such as in Table III can be properly compared only if the experimental conditions under which the measurements were made are defined. Work done in this laboratory indicates that it is possible for the sensitivity to vary by a factor as great as 10, depending on the manner of injection, the dilution of the sample in the carrier gas, the retention time of the sample, and perhaps other factors which remain to be explored.

One of two procedures may be adopted to standardize conditions for comparison purposes. The first involves the preparation of a standard column, packed with a standard liquid on a standard solid support, and the use of this column in a chromatographic apparatus whose conditions of operation are carefully defined: carrier gas flow rate, temperature, manner of sample injection, and size of sample. If now a standard sample material is decided upon, all the conditions for a valid comparison of detectors are defined. It is of interest to observe that Ray (*14*) and Boer (*2*) have proposed standard samples, although proposals to standardize other conditions for sensitivity determinations have not as yet been made. The procedure using a packed column has the drawback that it is difficult, if not impossible, to duplicate columns exactly with respect to important characteristics such as particle size of support, liquid-solid ratio, and packing density.

In the second procedure, which is recommended, the chromatographic process is dispensed with and an empty tube of standard length and diameter is used to connect the point of sample injection with the detector cell. The advantage of this procedure lies in the fact that it can be precisely reproduced from time to time and from laboratory to laboratory. It is recommended, therefore, that the following experimental variables be defined in measuring detector sensitivity: carrier flow rate, temperature, manner of sample injection, sample size, kind of sample, length and diameter of connection between injection point and detector.

Detectors have been described which use a particular carrier gas (*9*, *15*). For this reason it is not proposed to define the nature of the carrier gas but only its flow rate. The carrier gas is thus considered to be part of the detector system. Similarly, the amplifier, if any, and recorder are also to be considered part of the detector system.

TABLE III

SENSITIVITY AND LIMIT OF DETECTION OF SOME DETECTORS

Detector	S	R_n	Q_0	pQ_0	References
1. L&N therm. cond. cell	40,000	0.001	5×10^{-8}	7.3	*10*
2. Hot wire therm. cond. cell	40,000	0 01	5×10^{-7}	6.3	*6*
3. Thermistor	25,000	0 01	8×10^{-7}	6.1	*4*
4 Ionization gage	2.5×10^{6}	0.02	1.6×10^{-8}	7 8	*15*
5. Flame ionization	7.4×10^{10}	0.07	1.9×10^{-12}	11.7	*12*
6. Electric discharge	2×10^{10}	20	2×10^{-9}	8.7	*13*
7. Beta ionization	55,000	0.0125	5×10^{-7}	6.3	*2*

DISCUSSION

Standard experimental conditions such as proposed above were not used by the authors whose data are given in Table III. However, for the sake of bringing out some points of interest it is assumed that the experimental conditions were comparable.

Reference to Table III shows that, aside from the experimental conditions, the sensitivities of two detectors can properly be compared only when the noise levels are the same. When the noise level is not taken into account S may give an erroneous impression as to the capability of the detector. For example, Detector 6 appears to be more sensitive than Detector 1 by a factor of 5×10^5 when comparing S. When comparing Q_0, Detector 6 is more sensitive than 1 by a factor of only 25. This difference is seen to be directly related to the different noise levels. Similarly, Detectors 1 and 2 appear to have the same sensitivity when S is used, but Detector 1 is better than 2 by a factor of 10 when the Q_0 values are compared. Again, the difference is related to the noise levels. It is proposed, therefore, that in comparing the performance of different detectors that the limit of detection, Q_0, be used since the noise figure is implicit in this parameter, whereas it is not implicit in S.

Q_0 has another very important consideration in its favor. It corresponds very closely to the realities that exist in a gas chromatographic analysis. The detector is required to respond to the change that occurs from zero concentration of component in the carrier gas to the first appearance of the component. The detector then follows the increase in concentration to some maximum, but still quite small concentration, and then indicates when the concentration is again zero. Q_0 is the quantity that comes closest to describing the performance of the detector in this situation. S describes an unrealistic situation; rarely, if ever, is it required that a detector respond with 40,000 mv to a change of 1 mM/ml or with 1000 mv to a change of 1 mg/ml (*4*). Q_0 describes a physical situation which is of greater interest to the analyst using gas chromatography.

The use of exponential numbers can be avoided by using the proposed quantity pQ_0, as defined in Eq. (9). The p concept here is similar to that of pH which expresses hydrogen ion concentration. The pQ_0 values in the fifth column of Table III give a more easily grasped comparison than do the Q_0 values. Furthermore, the pQ_0 expression has the advantage of having larger numerical values associated with desired performance of the detector, while smaller values are associated with poorer performance.

SUMMARY

The conditions required for valid measurement and comparison of detector sensitivities in gas chromatography have been discussed. It is proposed that the experimental conditions to obtain the raw data be defined so as to validate comparisons of different detectors and of the same detector by different laboratories. The limit of detection is proposed as the parameter which is most useful in describing the sensitivity behavior of a detector and most useful for comparison purposes.

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CHAPTER IX

Compatible Readout System Design for Use with a Chromatographic Instrument Employing Golay Columns and Ionization Detectors

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Chromatography instruments currently in use normally employ a thermal conductivity detector and packed columns. A complete chromatographic system built upon such an instrument may, in addition to the instrument, comprise a potentiometer recorder plus one or more auxiliary devices (integrator, range changer, etc.). For such a system, or for any other system, it is apparent that of prime consideration is the ability of any readout device to display or operate faithfully upon all of the information contained at the output of the chromatographic instrument.

It is upon this general premise that the choice of the various readout instruments is made. In the contemporary chromatographic system using a thermal conductivity detector-packed column instrument, a number of commercially available recorders, integrators, and range-changing accessories adhere to this premise. Figure 1 shows a typical run from such a system. Recorders with a full-scale balance time of one second and integrators with a response time of the same order of magnitude as the recorder and with a full-scale count rate of a thousand or so counts per minute are adequate for present use.

The configuration of the system is such that the instrument output drives the potentiometer recorder directly, while integrators, range changers, and other elements are mechanically coupled to and actuated by the recorder.

This configuration is shown schematically in Fig. 2. In the figure, solid lines indicate an electrical linkage, and dotted lines a mechanical coupling. In this system, the integrator requires from the recorder a rotating shaft coupled to the recorder pen possessing adequate reserve power to operate the transmitting unit. This transmitting unit includes a potentiometer which serves as the input to the integrator plus a switch, also operated from the recorder shaft, which may serve to actuate auxiliary mechanisms in the integrator.

The range change unit similarly demands sufficient driving power from the recorder to operate its mechanism. It is, therefore, self-evident that in the present system, the strain clearly falls on the recorder.

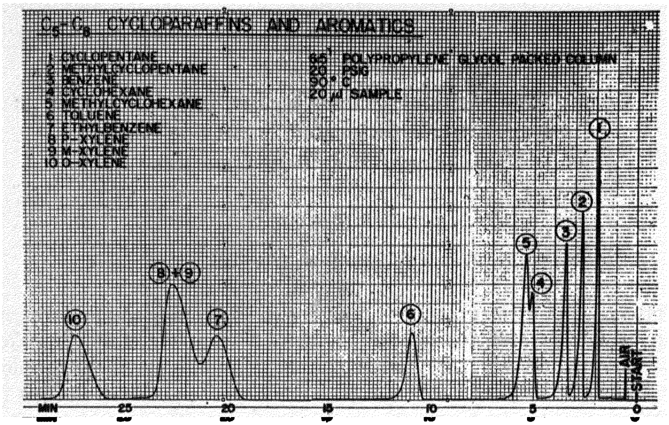

Fig. 1. Hydrocarbon run: packed column.

The potentiometer recorder is a highly accurate instrument, ruggedly constructed, and with sufficient reserve driving power to accommodate various mechanically linked accessories.

Its sole drawback in many applications is response time, which is limited to a maximum of about 0.25 seconds.

Recently, chromatography instruments have appeared which employ high-speed elements in their design; namely, ionization-type detectors and Golay (capillary) columns. These newer instruments, offering the advantage of higher speed data presentation, present a challenge to the operator who desires to utilize their full capabilities.

Acquisition of a high-speed instrument necessitates careful consideration of readout devices to be used in conjunction with the high speed chroma-

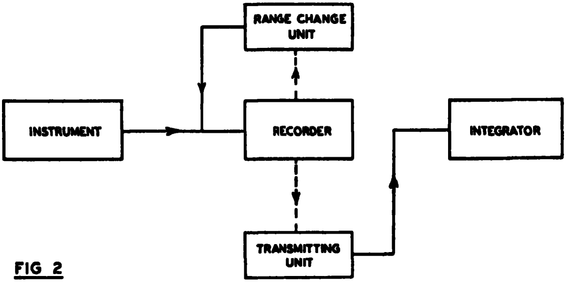

FIG 2

Fig. 2. Electro-mechanical readout system.

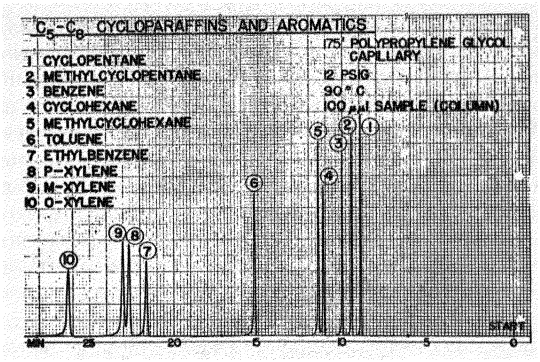

Fig. 3. Hydrocarbon run: Golay column.

tography unit. Rapidly eluted peaks, exhibited in Fig. 3, require fast response equipment to present useful quantitative data.

Beginning, then, with a chromatographic unit with ionization detector and Golay columns, and realizing the instrument's inherent capabilities, each element of the readout and display system must be evaluated on the basis of:

1. Its capabilities as an isolated element.
2. Its location in association with the other system elements.

The various types of ionization detectors in use in chromatographic instruments require a preamplifier to provide a signal of reasonable magnitude to drive a recorder or other display elements. The preamplifier is usually a DC electrometer type and for our purposes should be drift-free, linear within 1%, and have a response time in the 100 msec range.

The recorder for the proposed system should have a response time of at least one-tenth of a second. This requirement precludes the use of a potentiometer-type recorder and leads us to consider the galvanometer-type. The galvanometer recorder employs a meter movement-type coil in which the deflecting needle becomes a writing pen. The mass of moving parts is kept to a minimum and, consequently, speeds significantly higher than a potentiometer-type are attainable. These units contain delicate mechanisms so that mechanical attachment of transmitting potentiometers, limit switches, and the like is unthinkable. This facet of the high-speed recorder dictates a new system configuration in which no mechanical linkage to the recorder is permitted. Further, if we are to have the accessories as in the former system, an all-electronic data readout system is the obvious recourse. In this proposed system, the recorder is relieved of all responsibilities save that for which it is intended—the graphical presentation of the preamplifier output signal. Simultaneously, all other readout devices and accessories are actuated by this same signal. The preamplifier has now become the pivot point of the readout system. We may now amend the preamplifier's specifications with the additional requirement that it must also provide adequate and appropriate driving power for the accessories chosen.

The accessory equipment would include an electronic or electromechanical integrator accepting a voltage input. An integrator is necessary for accurate quantitative analysis of the output from the high-speed chromatographic instrument. The electronic- or electromechanical-type is required due to its high counting rate. Rapidly eluted peaks require a significant number of counts to be logged for each peak for precise quantitative study.

However, count rate per se is not meaningful unless the readability of the integrator is stated. Obviously, an integrator which can be read to an accuracy of one count and possessing a full-scale count rate of 5000 counts per minute is every bit as good as one whose count rate is 10,000 per minute and can only be read with confidence to two counts. But, if two instruments employ the same or similar display methods (counter, pips, etc.) the one with the higher counting rate is to be preferred.

The foregoing discussion presumes that the dynamic range (linear range of operation) of both integrators is comparable. If a discrepancy exists in this realm, analysis of individual instrument merit becomes more difficult and requires careful evaluation.

All electronic integrators using electronic-type counting and display tubes possess the advantages of extreme speed and high count rate.

It is questionable whether use of these ultraspeed instruments is justified in chromatography at present. Presentation and logging of data from these instruments require sophisticated and complicated auxiliary equipment to do full justice to their capabilities.

Velocity servo-type integrators are capable of faster response than a similar position servo mechanism (potentiometer recorder), although both may use the same rotating components. In a velocity servo, as opposed to a position servo, the rate of correction of an error is measured by the acceleration or deceleration rather than by the speed of the mechanical system. While the mechanical inertia of a system prevents any rapid change of speed, it does not prevent rapid changes of acceleration. Consequently, velocity servo-type integrators generally will fulfill the present requirements.

Further, an RC integrator at the input of the velocity servo mechanism can effectively store transient phenomena of short duration and enables the integrator proper to correct for transient, high-speed signals.

To summarize, dynamic range of the integrator should be large and response time should be comparable to the galvanometer recorder (0.1 seconds). Operationally then, the integrator should meet the above stated specifications.

An additional requirement, although not operational but of equal importance, is that of automatic data presentation. Proper logging of an integrator output by manual operations at high speed is difficult it not impossible. The rapidly eluted series of peaks from a high-speed chromatography unit dictate some form of automatic data-recording device. This device, acting upon the integrator's information, would display the integral of a peak permanently and at precisely the correct instant. The switch which performs this function of sensing the proper instant and displaying the integrator output would be operated from the preamplifier signal.

Assuming a digital counter-type display, two such counters could be arranged in the following manner. Counter A, after a band has been eluted, would have its number automatically printed upon a tape and immediately thereafter automatically reset to zero, thus logging a number associated with each peak. Counter B, with only a manual reset feature, would accumulate the total number of counts for the entire run. Its final figure would then also be transferred to the tape. Simple division would be required to obtained the useful information. The operator would thus be presented with a permanent record of the integral of each eluted peak during the run.

Accessories such as range-changing devices and other convenience elements may be incorporated in the readout system if desired. Such a device would automatically attenuate large signals by a preselected factor and would be of use in trace analysis. This unit like all others must possess rapid response characteristics. It would also be actuated by the electrical

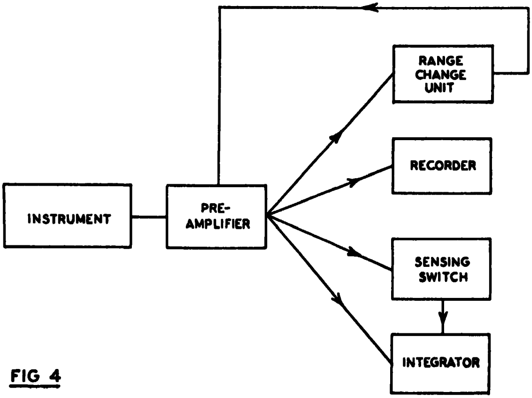

FIG 4

Fig. 4. Electronic readout system.

signal from the preamplifier. Figure 4 diagrams this system in schematic form.

It has been shown how basic design changes in chromatographic instruments necessitate careful choice of readout components and how entire system philosophy may be affected by these changes. Advances in the chromatographic field, particularly in the area of high-speed performance, will demand more sophisticated data systems capable of presenting data in convenient form with a maximum of speed and accuracy.

CHAPTER X

Performance Data on a New Ionization Detector

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In gas chromatography, a great deal of interest currently is being focused on detection methods. Developments of detectors with higher sensitivity have made high resolution separations more practical. Trace analysis can also take advantage of higher sensitivity providing, of course, the detector is able adequately to monitor the high concentration components.

There are numerous suggested methods of accomplishing gas chromatography detection in the literature. Several of these methods are rather well developed and are presently in use in laboratories throughout the world. Of these, thermal conductivity is perhaps the best known. It is quite reliable, has moderate sensitivity, and is, in fact, regarded almost as standard. Despite its limitations, thermal conductivity is adequate to handle a large proportion of the samples subjected to routine analytical work. It, therefore, undoubtedly will continue to be a valuable tool.

In general, detectors may be divided into two categories: those which respond to a property of the carrier, and depend on a change in that property when the sample mixes with the carrier; and those which respond to a specific property of the component, and are independent of the carrier. Thermal conductivity falls in the first category. One of those falling in the second is ionization. It is a fortunate circumstance that the ionization potentials of most organic compounds fall below those of the commonly used carriers. Ionizing the sample component and measuring the resulting ion current is a convenient and sensitive means of detection.

Table I shows the ionization potential for various materials and the excitation potential for argon.

The usual elements of an ionization detector consist of a source of energy producing free electrons, which then may ionize the sample, or excite the carrier to a metastable state which, in turn, ionizes the sample; a potential field to move the ions; and a measuring circuit to convert the ion current into a recorder signal. Several systems have been created on this basis, differing mainly in the source of the energy used to produce ionization. Deal *et al.* (*1*), describes such a detector based on beta emission of strontium-90 and using nitrogen as the carrier. Lovelock (*2*) utilizes a similar system, except that argon is used as the carrier gas and advantage is taken of the metastable state of argon to yield increased sensitivity. The flame ionizer of McWilliams (*3*) gets its energy from the oxidation process. The electrodes in the flame monitor the ion current in the conventional fashion. Karmen's (*4*) radio frequency detector appears to operate upon a somewhat different basic arrangement. With it, ionization is carried to a point where background current of considerable proportion is established, and the sample component reduces this level. Excellent results have been reported for this detector. Ryce and Bryce (*5*) describe an ionization gage type detector with the energy supplied by electron emission from a filament. Electrons are accelerated to ionizing energy by a positive potential, and the ionization current, caused by the positive ions, is measured. It is operated at reduced pressure.

The detector described in this paper is based on the same principle as the detector of Ryce and Bryce. This type appeared attractive for its high sensitivity with relative freedom from temperature and flow effects and complete absence of radiological hazard. In addition, any compound could be handled.

Figure 1 shows a block diagram of the analytical arrangement of the new ionization detector being presented.

A conventional carrier and either packed or capillary columns are used. At the outlet of the column, the effluent stream is divided by a take-off control which sends a portion to the ionizer and the balance to the atmosphere. The area labeled "Ionizer Electrical Controls" contains the circuitry necessary for supplying the various voltages required for the filament and collector. Electrons necessary for ionization are supplied by a filament and

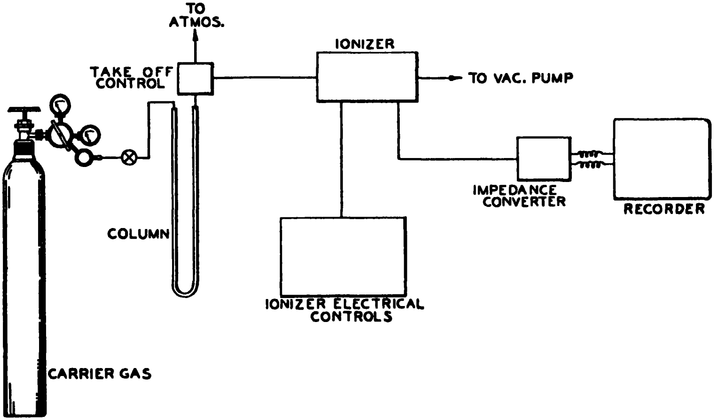


FIG. 1. Diagram of analytical arrangement of ionization detector.

are accelerated by a positive charge. The positive ions formed are collected by means of a negative potential. Ionizing energy is maintained below the energy necessary for ionization of the carrier itself. When the effluent stream enters the detector carrying a sample component, ions are produced, which are attracted toward the negatively charged electrode, thus setting up an ion current. A voltage is developed by this current across a signal resistor, and is fed to an impedance converter which changes the high impedance signal to the low impedance needed to operate a standard potentiometric recorder.

In the instrument design, much emphasis has been placed on producing a simple, practical device. An ionization tube specially designed for gas chromatography provides stability and long life. An ordinary vacuum pump is all that is required for operation.

Carrier Gases Used

Helium, argon, hydrogen, nitrogen, and carbon dioxide were all tried as carriers. All can be used, but each has characteristics which make the particular choice depend upon the application. Helium and argon have the greatest sensitivity and appear to be best.

With helium, a direct ionization of the sample occurs with electron energies below the ionization potential of helium. Advantages are high sensitivity and linearity of response over wide concentration ranges. No sample component has been found which could not be handled by the use of helium as the carrier. With it, all of the materials outlined in Table I can be determined. The maximum ionizing energy that can be used is about 18 volts before the background becomes excessively high. This also was pointed out by Ryce and Bryce. Higher energies probably can be used with resulting increase in sensitivity, when helium with a higher purity is available.

Argon can also be used as the carrier. The principle advantage of argon is an increase in sensitivity over helium. The use of argon results in an enhancement in sensitivity due to the formation of an excited state produced at an energy just above the excitation potential for the argon. Using the same energy for argon and helium, an increase in sensitivity of approximately 100 is observed. However, since helium can be used at a much higher ionizing energy, the actual increase is a factor of about 2 to 5. As more pure helium is available, it is believed that helium eventually will have the greater sensitivity.

There are two disadvantages in the use of argon. First, the compounds above ethylene in Table I either are not obtained or are obtained with greatly reduced sensitivity. Second, argon is linear over a narrower concentration range. The argon is sufficiently linear for all capillary column work and only becomes nonlinear in the larger sample ranges. Both argon and

TABLE I

IONIZATION POTENTIAL FOR VARIOUS MATERIALS AND EXCITATION POTENTIAL FOR ARGON

Material	Ionization potential
Helium	24.6
Argon	15.7
Hydrogen	15 6
Nitrogen	15.5
Carbon dioxide	14 4
Methane	14.4
Carbon monoxide	14 1
Ethane	12 8
Water	12.6
Oxygen	12.5
Acetylene	12.3
Cyclopropane	11.8
Ethylene	11 5
Argon (metastable)	11.5
Paraffins (C_3–C_{10})	10 5–11 2
Cycloparaffins (C_4–C_6)	10 5–11 0
Alcohols (C_1–C_3)	10.1–11.0
Aldehydes	10 0–11 0
Ketones	9 7–9 9
Olefins (C_3–C_6)	8 4–9 8
Aromatics	8 3–9 5

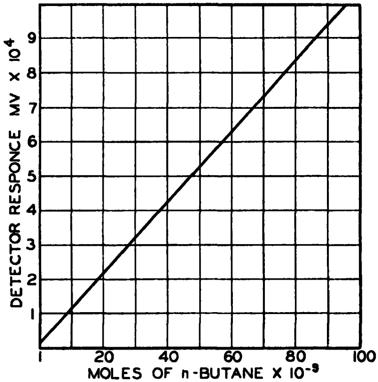


FIG. 2 Calibration curve from packed column for *n*-butane, using helium as the carrier.

helium have been used successfully as carrier gases, with helium having the wider application.

Regarding the use of carbon dioxide, hydrogen, and nitrogen with ionization potentials of 14.4, 15.6, and 15.5 ev, respectively, all can be used at

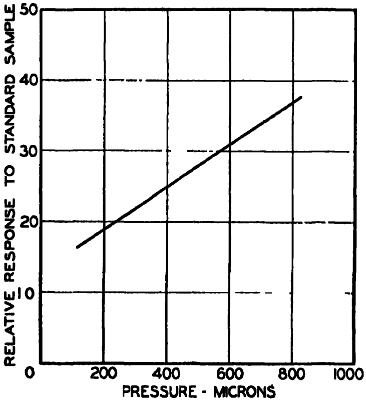


FIG 3. Effect of variation of ion tube pressure for helium.

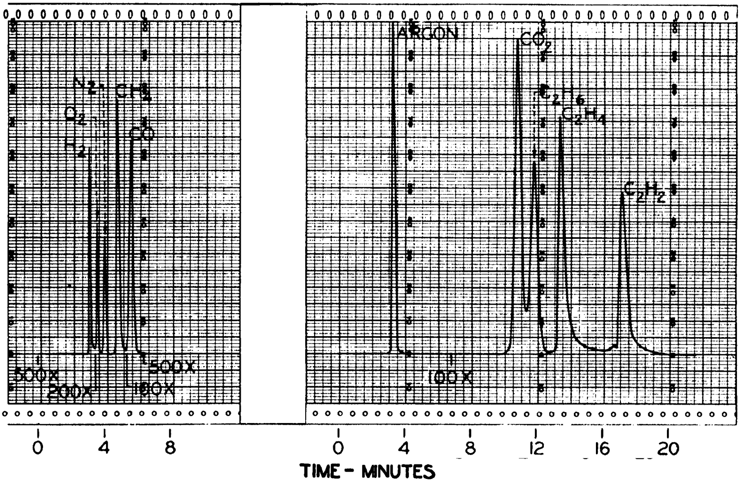


FIG. 4 Analysis of fixed gases on a molecular sieve (left) and silica gel (right).

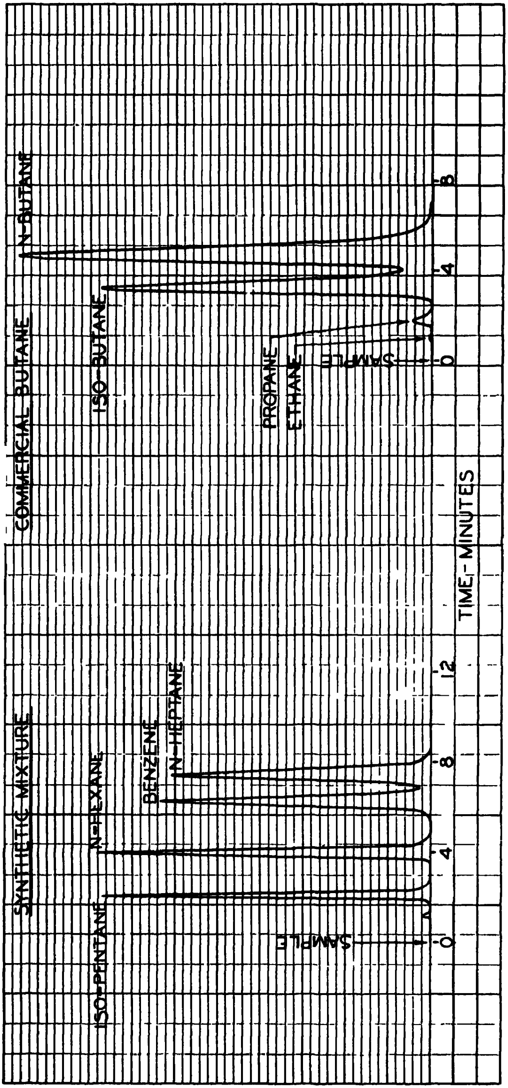


FIG 5 Analysis of a synthetic mixture and of commercial butane on a packed column (3 mm ID)

ionizing energies below these levels. However, there appears to be no advantage over helium and there is a considerable reduction in sensitivity.

CALIBRATION

This new ionization detector has been found to give a linear response over wide concentration ranges.

Figure 2 shows a typical calibration curve from a packed column for *n*-butane, using helium as the carrier. A gas phase sample was used for calibration because of the high accuracy of measurement and convenience in preparation.

SENSITIVITY

Sensitivity in terms of the Dimbat, Porter, and Stross (*6*) equation gives an S value of 10^6. This really represents the potential sensitivity, rather than the actual, because the noise level of ionization detection is inherently higher than that of thermal conductivity. Sensitivity at least 1000 times that for thermal conductivity was obtained and this figure can be greatly improved as better ways for noise elimination are found.

Sensitivity is adequate for capillary columns as well as microsamples in packed columns.

RESPONSE TIME

Since the effective detector volume at 100 μ pressure is approximately only 7 μl, response time is extremely fast and satisfactory for all applications.

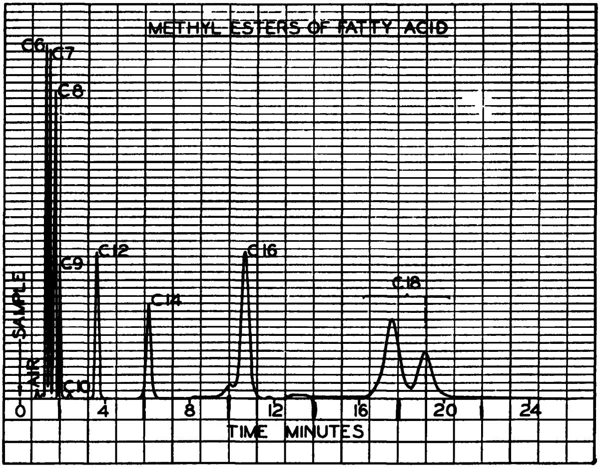
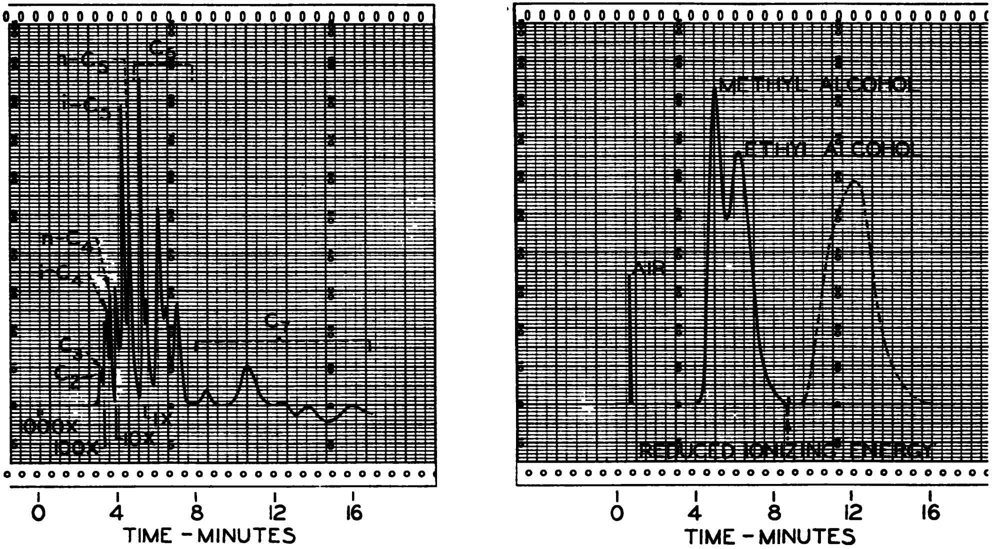


FIG. 6. Analysis of fatty acid esters on a packed column.



(A) (B)

FIG. 7 Analysis of a natural gas mixture (A) and of water-alcohol mixture (B)

EFFECT OF TEMPERATURE, PRESSURE, AND FLOW

The detector pressure is not critical as long as it is held within reasonable limits. Operation usually is in the region of 1/10 to 1 mm.

Figure 3 shows the effect for helium of variation of ion tube pressure over a range of 1/10 to 1 mm.

The device is insensitive to changes in temperature, as indicated by Ryce and Bryce.

Base lines are unaffected by changes in carrier flow. Since the flow does determine the sample-to-carrier ratio entering the detector, the flow should be maintained constant during the analysis period.

ANALYTICAL RESULTS

A number of typical determinations are shown.

Figure 4 shows the analysis of fixed gases on a molecular sieve (curve on left) and silica gel (on right) for the determination of hydrogen, oxygen, nitrogen, methane, carbon monoxide, argon, carbon dioxide, ethane, ethylene, and acetylene.

It is interesting to note that the hydrogen is obtained with high sensitivity and as a positive peak, so that the problem of determining hydrogen is not present as it is in thermal conductivity measurements. Sample sizes of the order of 0.05 ml gas were used.

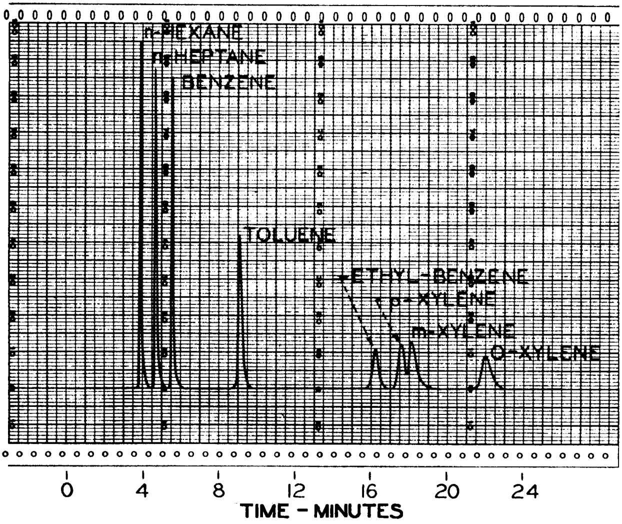


FIG. 8. Capillary column analysis of a synthetic aromatic-paraffin mixture.

Figure 5 shows the analysis of a synthetic mixture and commercial butane on a packed column of 3-mm inside diameter.

Figure 6 is the analysis of fatty acid esters, also on a packed column. When using helium, advantage can be taken of the differences in the ionization potentials to effect certain desired analytical results. As an example, Fig. 7(A) is the analysis of a natural gas mixture. In this analysis, the ionizing energy was set below that for methane, but sufficiently high to ionize all components with lower ionization potentials. Using this technique, the small concentrations of C_5, C_6, and C_7 were easily picked out. A modification of this technique is shown in the same figure (B) for the analysis of methyl and ethyl alcohol in water. Water concentration was above 90%. The ionizing energy was set to obtain the alcohols, and then reduced after the alcohols to block out the water. The attenuated water peak that would have been obtained at a higher energy is shown by the dotted line.

An ionizing energy between alcohol and water could have been used. Due to the small difference in potentials (H_2O at 12.6 and methyl alcohol at 11.0) it would not be possible completely to block out the water, but it would have been determined with much reduced sensitivity. Where greater differences occur, as in the natural gas (CH_4, 14.5 and butane, 10.97); the technique is more effective in blocking out the major component.

The detector proved very satisfactory for capillary columns

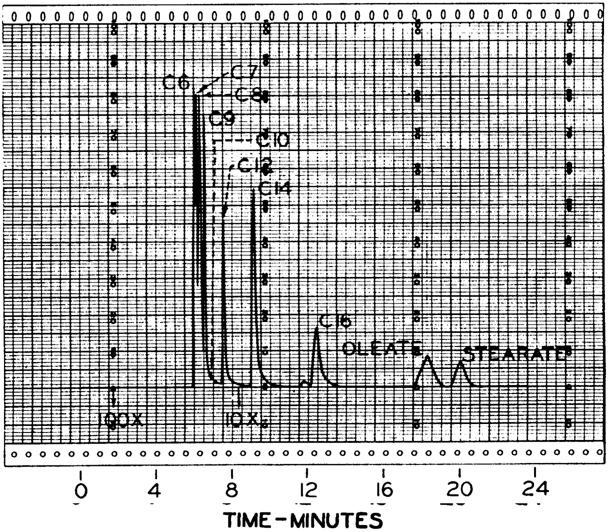


FIG 9. Analysis of methyl esters of fatty acids on a capillary column.

Figure 8 is a typical capillary column analysis of a synthetic aromatic-paraffin mixture and shows the separation of the xylene isomers.

Figure 9 is an analysis of methyl esters of fatty acids on a capillary column.

CONCULSION

A simple, new ionization detector has been developed. Electrons for ionization are supplied by emission, providing high sensitivity, simplicity, and linear response for gas chromatographic analysis of moderate and small size samples. The detector is relatively insensitive to small changes in temperature and pressure. Flow may be interrupted for sampling, but must be held constant during the analysis. The detector is suitable for use with capillary columns or packed columns. Helium and argon are the preferred carrier gases. The maximum sensitivity is obtained with argon as the carrier, but it has the disadvantage that fixed gases and low molecular weight hydrocarbons either are not obtained or are obtained with poor sensitivity. No sample component has been found that could not be analyzed with helium as the carrier. Ready control of the ionizing energy provides the flexibility for many special techniques.

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CHAPTER XI

Process Control Systems Embodying Gas Chromatography Analyzers

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The features necessary in a process-type gas chromatography, and the possibility of employing the chromatograph in a process control system, were discussed at the International Symposium on Gas Chromatography* in August of 1957 by Mr. B. O. Ayers of Phillips Petroleum Company. At that time, commercial process analyzers were in their infancy, although several instrument manufacturers were offering them, and many others were keenly aware of their potential. In the intervening two years the number of process gas chromatographs has risen rapidly. At the present time several hundred of these instruments are installed, or are being installed, in process industries.

In general, the performance of these analyzers has been good. The experience and technical competence of instrument manufacturers and users have combined to allow maximum performance with a minimum of maintenance. A natural result of this satisfactory performance is the extension of the gas chromatographic technique to automatic control of process operation. At the present time there are in the field many units which have been designed for process control.

Figure 1 is a block diagram of the chromatographic control system. The attenuated output from the analyzer is fed to a transducer, which converts the small electrical signal to a pneumatic or electrical output of the desired amplitude. Because of the intermittent presentation of chromatographic data, some method of storing information must be incorporated. Once the intermittent signal has been converted into a continuous signal (pneumatic or electrical) it can be used in a control system in any conventional manner. The preferred manner seems to be to use the signal to adjust the set point of some other control, such as temperature or flow controller, in what is known as a cascade control system.

ELEMENTS OF A PROCESS CHROMATOGRAPH ADAPTED TO PROCESS CONTROL

Essentially, the elements which have been added to the conventional analyzer to adapt it to process control are: (1) a transducer and (2) a means

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* See B O. Ayers, *in* "Gas Chromatography" (V. J. Coates, H. J Noebels, and, I. S. Fagerson, eds), pp. 249–266. Academic Press, New York, 1958.

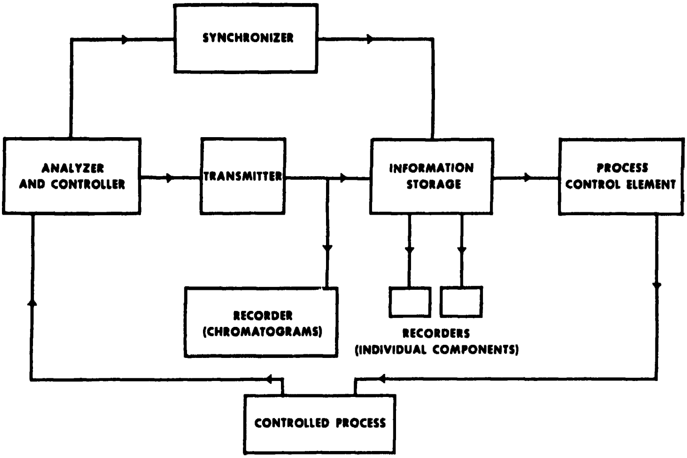

FIG 1. Block diagram of chromatographic control system.

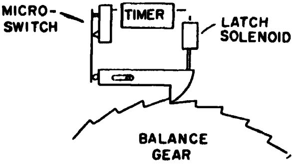

FIG 2 Schematic peak picker.

of reading out and storing the information represented by the transducer output.

The transducing element is a conventional electrical-to-pneumatic or electrical-to-electrical type. Since the chromatographic peaks, and hence the transducer output, are transitory, it is necessary to introduce an arresting device. Figure 2 illustrates a simple mechanical device which can perform the function of "peak picking." The purpose of the peak picker is to "freeze" the transducer output for the length of time required to transmit the information to a storage element. When the solenoid is energized, the clutch on the actuating arm follows the perimeter of a notched wheel, which is usually attached directly to the indicator dial of the transducing element. The wheel and clutch are designed so that when the indicator reaches a peak maximum and the direction of rotation tends to reverse, the clutch engages in a notch and prevents movement. The wheel can be held in this

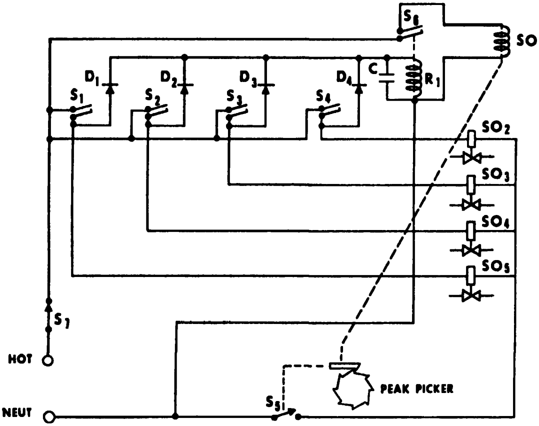

FIG 3. Schematic synchronizer

position as long as required. As the torque of the balancing motor is applied to the actuating arm, the arm moves slightly and closes a microswitch.

Figure 3 is a schematic diagram showing one manner in which the peak picker can perform its functions. The switches S_1–S_4 are associated with the timer motor which programs the operation of the chromatograph. They are actuated in turn as the sample components of interest emerge from the chromatograph. Each of these switches is in series with a corresponding solenoid valve which (in the pneumatic system) controls the flow of air to air-operated valves. These air-operated valves control the flow of air from the transducer to the appropriate storage vessel. (In the electrical storage system these switches are in the leads to the storage condensers.) These switches do not actuate the solenoid valves, but simply select the valve which will be actuated when the peak picker switch is closed.

SO_1 is the solenoid which engages the peak-picking mechanism. It is actuated by the relay R_1, which is energized through the switches S_1–S_4. One of these switches closes as each measured component emerges from the chromatograph. When the peak is reached, the microswitch S_5 closes, the appropriate solenoid valve is actuated, and the storage vessel charges or discharges as dicated by the transducer output. The capacitor C holds relay R_1 closed for a short period after each of the switches S_1–S_4 opens, to allow the pneumatic valves on the storage vessels to close. The relay then releases and the actuating arm is disengaged. Thus, as each component of interest emerges from the chromatograph the appropriate storage vessel is selected, charged, and isolated.

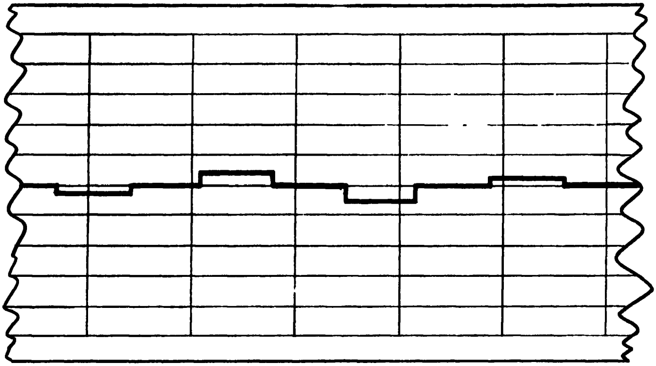

FIG. 4. Recorder presentation of continuous signal from gas chromatograph

In the electrical system the element corresponding to the pneumatic storage vessel is a capacitor. A high-grade, polystyrene-insulated capacitor, in the grid circuit of an electrometer tube, will retain its charge virtually unchanged for periods of time much longer than the period between chromatographic analyses. Two relatively large capacitors are used. While the potential on the first is being employed in the control system, the second capacitor is discharged, in preparation for recharging on the next cycle of the chromatograph. A third capacitor, small relative to the first two, maintains the output during the switching between the two large capacitors.

In this manner the intermittent output of the chromatograph is transformed into continuous pneumatic or electrical signals of proportionate size. These penumatic signals may be recorded (in the form of a stepwise function, as in Fig. 4), and used directly in process control.

APPLICATION OF CHROMATOGRAPH CONTROL SYSTEMS

The list of applications for which control systems have been engineered is becoming quite sizable. The fractionation units of alkylation plants and refineries are demanding a variety of systems; for example, control of the ethane or propylene content of absorber off gas, and, in general, of the key components in column distillations. Systems have been provided for demethanizer, de-ethanizer, depropanizer, and debutanizer columns, in some cases controlling on the basis of "heavy" components in the overhead and in others on "light" components in the bottom stream. Ethylene plants have been provided with control systems for several different applications.

One control system of more than ordinary interest from the point of view of application engineering, is a sulfur recovery plant installation. In the process of sulfur recovery, the H_2S (which accounts for a very large part of the sulfur present), is partially oxidized and catalytically converted to free sulfur according to the following equations:

$$H_2S + \tfrac{3}{2}O_2 \rightarrow H_2O + SO_2$$

$$2H_2S + SO_2 \xrightarrow[\text{(Catalyst)}]{} 3S + 2H_2O$$

In order to optimize the recovery of sulfur, it is important to control the ratio of oxygen to hydrogen sulfide in the first step of the process. It is desirable that $\frac{1}{3}$ of the H_2S in the feed be converted to SO_2, so that the H_2S/SO_2 ratio in the second step will be stoichiometrically correct. In practice it is convenient to measure the unreacted H_2S and SO_2 in the process tail gas, and control the addition of air on the basis of the H_2S/SO_2 ratio.

In addition to the unreacted H_2S and SO_2, the tail gas contains large quantities of water vapor, and some entrained sulfur. Several per cent of CO_2, and small amounts of hydrocarbons through propane, are also normally present. It is necessary that the sulfur be removed before the sample reaches the analyzer. The water content must not be reduced, since appreciable quantities of SO_2 would be lost with it. Moreover, the presence of water prevents further reaction in the sample system. The sampling point is at approximately atmospheric pressure. This combination of conditions makes the sample handling problem a difficult one.

The problem has been satisfactorily solved in the following manner: A steam jet exhaustor is used to draw the sample through a sulfur removal system, which is essentially a "cooler" maintained at 212°F, and thence to the analyzer. Sample lines, components of the sample handling system, and the analyzer itself are maintained at elevated temperatures. The system is designed to have a minimum of resistance to flow, in order that the pressure in the analyzer shall be close to that at the sample point. If the sample point pressure is subject to variations, a pressure regulator is included to maintain a constant pressure in the analyzer.

It is necessary in setting up the analysis to present the H_2S and SO_2 peaks in positions where there is no interference from any of the other components present. The dual column arrangement affords a very satisfactory solution to the problem of handling the large amount of water present and at the same time minimizing the time required for the analysis. In this arrangement, the low boiling components are allowed to proceed through the first column into a second column where they are stored. Continued flow of carrier gas through the first column only removes the water from that column in a short time. The necessary separation of H_2S/SO_2 from the other components is then performed in the second column.

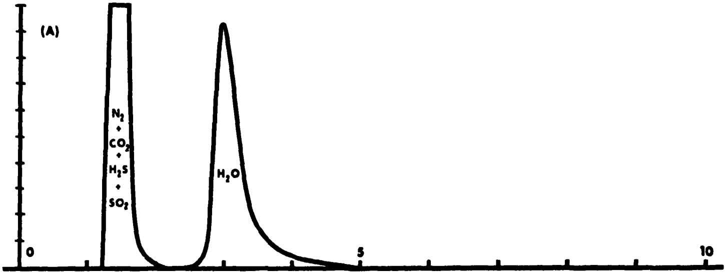

FIG 5 (B)

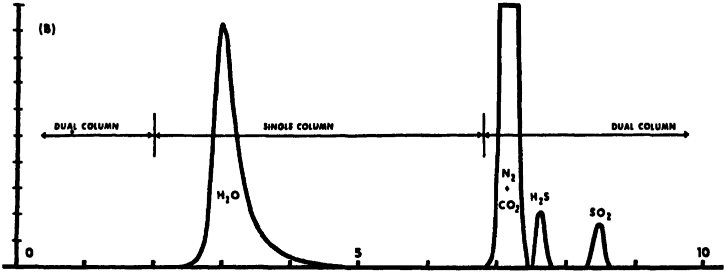

FIG 5 (A) A short No. 1 column separates H_2O from the lower boiling components (B) Dual column operation gives rapid elution of H_2O from the first column; then H_2S and SO_2 are separated from air and CO_2 in the second column

The first column is a short length (about 2 ft) of Carbowax 400 on 60–80 mesh Celite. The second column is 16 ft long, and contains di-isodecylphthalate on C-22 firebrick (42–60 mesh). Figure 5(A) shows how the water is separated from the other components in the first column. Figure 5(B) shows how the dual column operation is programed to discard the water peak and present the H_2S and SO_2 in positions where there are no interfering components.

The outputs corresponding to the concentrations of H_2S and SO_2 are fed into a ratio relay which produces a signal proportional to their ratio. This is the signal which is used to adjust the flow of air to the process, and thus maintain the H_2S/SO_2 ratio at the desired figure.

GENERAL REMARKS

In control system, performance requirements placed on the chromatograph are exacting. It is imperative that the system operate on a trouble-free basis for long periods of time. This severely restricts the number of suitable partitioning liquids, since the vapor pressure of the liquid must be so low that the elution time of sample components will not change over a period of several months. In addition, if the process has a short time lag, it is necessary to minimize the period between analysis in order to obtain maximum benefits from the control system. The necessity of providing analyses in the parts-per-million range in certain applications, such as those found in the ethylene plant, puts further pressure on the instruments engineer.

All of those performance requirements are being met with a least moderate success. It would be misleading, however, to imply that the chromatograph control system is either simple or entirely trouble-free. Most, if not all, of the present installations are in large plants, and under direct supervision by well-trained engineering or instruments personnel. Regular maintenance and testing of the system is required. Installation and start-up are engineered by the manufacturer, and continuing contact with each installation is maintained by the manufacturer's field engineers. All of these services are necessary to obtain maximum performance from the system.

CHAPTER XII

An Improved Recording System for Gas Chromatography

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INTRODUCTION

The increasing importance of gas chromatography as an analytical tool has caused considerable effort to be directed toward simplification of data gathering and reduction. Several features contributing to this aim have been incorporated into a recording system designed and built at the Gulf Research & Development Company's laboratories.

A mechanical integrator, responsive to the function being recorded, and whose output is coupled to a second pen, charts directly the time integral of the thermal conductivity cell output. A pen-drive, incorporating a reversing screw, allows the function pen to traverse the chart five times in covering the full range of the recorder, thus greatly increasing the amount of usable data. A similar pen-drive continuously follows the integrator output, permitting the total value of any integral to be recorded. Many of the maintenance problems commonly encountered in the use of conventional potentiometric recorders have been avoided by operation of the entire system on 60-cycle, 115-volt AC. Eliminated from the recorder by this expedient are: the recorder working battery and standard cell, the standardizing system, and the input chopper and its associated circuitry. A further gain is achieved by the substitution of a voltage-regulating transformer for the previously required source of regulated DC used as excitation for the thermal conductivity cell.

INSTRUMENTATION

General

Several factors influenced the design of the recording system about to be described. Two time consuming operations were chosen for intensive study: (1) the conventional methods of measuring and calculating peak areas, and (2) the constant operator surveillance necessary to attenuate properly the large peaks, and yet maintain sufficient system sensitivity to record small events. Freedom from certain routine maintenance procedures, and unpredictable battery failure also weighed heavily in the choice of the present design.

Preliminary Recorder Designs

The design trend which was followed may perhaps be better appreciated after a brief resume of the limitations which affected the utility of some previous models. Time integration of the conductivity cell output was achieved by the incorporation of a mechanical integrator whose disc drive is obtained from a synchronous motor (the recorder chart motor), and in which the ball cage is positioned by a micrometer screw, which in turn is rotated by the pen positioning mechanism. The rotational output of the integrator is mechanically linked to a lead screw which causes a second pen to traverse the recorder chart. This expedient serves quite well for many reasonably predictable analyses but is limited both in its scope of compatible samples and by the numerical value of the integral which can be recorded.

The problem of presenting both small and large peaks on the same chart was attacked by the addition of an auxiliary potentiometric circuit which introduces discrete increments of voltage opposing the output from the thermal conductivity cell. These increments of electromotive force (emf) are added or subtracted from the recorder input by impulses from the recorder limit switches and other appropriate circuitry. Since this type of operation involves sudden pen excursions in the directions to accommodate the abrupt changes in recorder input, it is obviously incompatible with the previously mentioned recording integrator.

To circumvent this problem and to provide a recorder combining the folded scale feature and the integrator in one unit, a major departure from normal design was made. In this model a multiturn slide wire was combined with a reversing-screw pen-drive to effectively increase its scale width five times. In this connection it should be mentioned that a spread of five scale lengths was chosen, since this approached the limits of resolution of the slide wire and the integrator, and, thus, was in no way determined by the reversing screw: i.e., the reversing screw is capable of a virtually unlimited number of traverses. The integrator, in this case, is driven as before but its output is also coupled to a reversing-screw pen-drive. This feature allows recording any numerical value reached by the integral during the course of a run. Furthermore, any suitable integrator scale factor may be obtained by simply changing the ratio of the gear train driving the integrator disc. From a data-gathering standpoint this recorder has been very satisfactory and has been in continuous service for some eighteen months; however, as the need for more instruments developed it was decided to try to eliminate some of the disadvantages inherent in potentiometric recorders. This decision resulted in the present instrument.

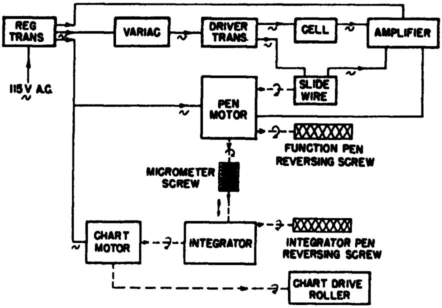

Fig 1 Block diagram showing parts comprising entire recording system

Final Recorder Design

The basic layout of the current instrument is shown in the block diagram, Fig. 1. Mechanically, it is essentially the same as the last model mentioned; the chief difference being that it lacks the mechanism necessary for standardizing the potentiometric circuit. This, of course, became unnecessary since the slide wire is electrically in the bridge circuit. Purchased parts, i.e., gears, bearings, etc., are used insofar as they can be adapted to the requirements. The reversing screws are specially made and their pitch, diameter, and material are largely a result of compromise between the ideal and the practicable in design. Their lead is 0.2 inch with a total length of 10 inches and the thread depth is 0.045 inches. They are made of brass for easy machining and are chrome-plated for durability and corrosion resistance. In order to reduce backlash and ensure smooth operation, the prototype reversing pawl was hand-fitted, then displayed on an optical comparator to establish its dimensions for production. As a result of this design procedure, the "turn-around error" is for most purposes negligible; in this case being about 0.015 inches of total chart travel. Another feature of this instrument, which is a result of a long-felt desire of the author, is that the mechanical portion of it may be completely removed from the case and placed upon a workbench where it remains in stable equilibrium and is readily accessible.

Alternating current operation was attempted in an effort to reduce routine maintenance and to eliminate the need for a closely regulated DC supply for the thermal conductivity cell. Further apparent advantages lay in eliminating both the thermal emf's in connections and the triboelectric effects in the slide-wire itself, which arise from the single moving contact in commercially available potentiometers. These voltages seriously affect the near-balance performance of a DC potentiometric recorder.

A routine and very effective means of measurement is that of comparing one quantity with another. This is done automatically in the conventional potentiometric recorder. As is well known, the emf in the potentiometric circuit is first compared and then adjusted to conform with that of a standard cell; it is then in turn compared with and balanced against an unknown potential. This procedure, while being almost universally applicable and useful, seems in some cases to become needlessly involved. This line of thought was followed during the consideration resulting in the recording system being discussed. Properly chosen resistors are perhaps the most stable of the "workhorse" variety of electronic components and, as such, assume the principal responsibility for stability in the gas chromatographic system being described. In this circuit the slide-wire, which is a portion of the thermal conductivity cell bridge, is supplied by the same source of potential as the cell units; therefore, any supply voltage variations resolve themselves into second-order errors instead of appearing directly as they do when separate sources of potential are involved. Theoretically the only error, due to supply voltage, may be caused by differences in the resistance-current characteristics of the cell elements themselves. The presence of such unavoidable mismatch in the cell elements prompted the use of a regulating transformer which has a low value of harmonic content in its output. This factor assumes importance since, as is well known, many voltage-regulating transformers produce a relatively high percentage of harmonic components, which although not evident in ordinary voltmeter observations, represent quite a large portion of the total watts involved. These harmonic components, since their magnitude changes with input voltage fluctuations, can result in varying heat in the cell elements, thus causing erratic recorder output. A variable autotransformer is used between the regulating transformer and the bridge excitation transformer in order to establish the proper operating level. The driver transformer is a carefully balanced, electrostatically shielded unit, chosen to minimize reactive unbalance of the bridge.

The cell-slide-wire bridge is shown in Fig. 2. It incorporates means for recorder range changing, along with appropriate amplifier gain settings,

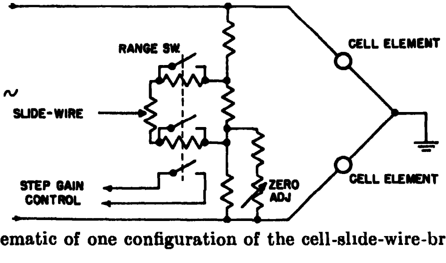

FIG. 2. Schematic of one configuration of the cell-slide-wire-bridge circuit.

and also provides a zero adjustment for the bridge. In order to properly set and observe the base line the recorder zero must necessarily be upscale from the left-hand stop, which requirement demands that two properly chosen resistors be added to or removed from the circuit when the range is changed. This is necessary not only to facilitate reading the chart, but also to maintain consistent integrator output since it is governed by the position of the function pen.

The output of the cell-slide-wire bridge is fed into a high gain amplifier

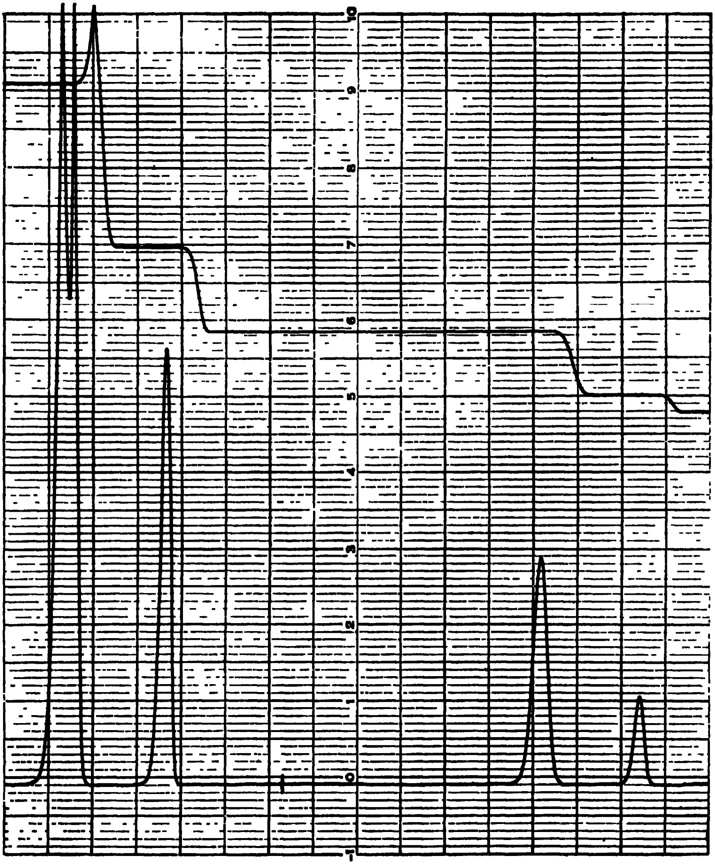

FIG. 3. Typical recorder chart showing several peaks and their respective integrals.

suitable for supplying power to one winding of the pen-drive motor. Commercially available plug-in units comprise the voltage gain portion of the amplifier, which results in lower construction costs and simplified maintenance. Only a few features distinguish this amplifier from any other which might serve the same purpose; one being the method of side-stepping a serious decoupling problem. It was found that if two plate voltage supplies, one using a vacuum tube rectifier and the other having solid state diodes, were operated from the same power transformer their respective time constants were such that effective decoupling was achieved with a minimum of components. Nonlinear feedback from the variable phase of the pen-drive motor into the amplifier is utilized to stabilize the servo loop. The principal advantage of this form of feedback is that it has relatively little effect, signalwise, while the servo motor is "slewing" but builds up in percentage of total signal as the voltage across the motor winding decreases. This form of feedback avoids the use of a more expensive motor generator and is adequate for this application.

The pen motor is a conventional two-phase induction motor which drives the reversing screw to position the pen and the multiturn slide-wire; it also rotates the micrometer screw. Appropriate gear trains link the various units, and since there are no strings or cables in the system, the only foreseeable maintenance is occasional gear cleaning. Microswitches are pro-

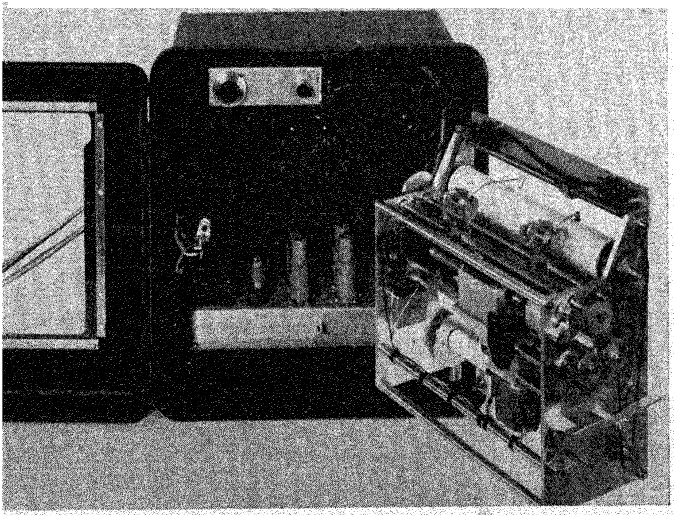

FIG 4 Photograph of recorder assembly.

vided to reduce the power to the fixed phase of the motor when the slide-wire approaches either end of its travel. This prevents jamming and possible damage to the gear train and slide-wire.

Translational motion is given the integrator ball cage by a modified micrometer screw, as indicated in Fig. 1. The chart motor drives both the integrator disc and the chart drive roller through appropriate gear trains.

One of these units has been in operation for approximately six months and has performed satisfactorily in conjunction with a heated wire-type cell. Figure 3 shows a chart which is typical of many runs. Figure 4 is a photograph of the complete recorder, showing its essential features.

SUMMARY

A recording system which greatly facilitates routine gas chromatographic work is described. The output of the thermal conductivity cell is recorded by a two-pen recorder upon whose chart is also traced the time integral of the function. Instrumentation and maintenance are considerably simplified by a new design in which the recorder rebalances directly the cell bridge circuit. Further simplification is obtained by the use of AC to excite the cell.

CONCLUSIONS

It is believed that, considered as a special instrument, this recording system has many advantages over conventional instruments, chief among these being reduced maintenance and the method of presenting the data. Several months' use indicates that both the operation and data reduction processes are considerably improved by this system. The experience gained from the development work just described may well point the way to further improvements. It appears that any great increases in instrument sensitivity must be accompanied by improved effluent control and by the elimination of temperature gradients in the apparatus. Vibration of the cell may become a problem in some installations but can probably be mitigated by proper shock mounting and isolation.

ACKNOWLEDGMENTS

The author wishes to extend his thanks to the Gulf Research & Development Company for permission to publish this paper, and especially to Mr. R. D Wyckoff, Dr. N D. Coggeshall, and others who rendered aid and assistance

CHAPTER XIII

A Precision Integrator for Gas Chromatography

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PRECISION REQUIRED

Well-designed chromatograph equipment will allow two succesive runs of the same sample to be reproduced within the thickness of a pen line. Since a pen-line width usually represents about 0.2% of the full-scale pen travel, it can be assumed that the reproducibility of the equipment is in this order of magnitude. When an integrator is added to the system it is imperative that it not diminish this degree of precision. Accordingly, the integrator should be able to compute and record the actual chart areas within an order of magnitude better than 0.2% (0.1% full-scale) if the precision of the chromatograph is to be retained.

DESCRIPTION OF INTEGRATOR

Figure 1 shows a newly designed ball and disc-type mechanical integrator installed on a standard recorder. Installation is fairly simple and may be accomplished on most existing recorders in the laboratory.

Figure 2 is a schematic, showing the operation. The input is taken directly from the recorder pen drive system by a mechanical connection. The time input is supplied by a clock-type synchronous motor. A heart-shaped cam on the output shaft within the integrator provides the motion to drive a pen back and forth on the chart. As the chart moves, the pen draws a pattern consisting of a series of small peaks.

Figure 3 shows the method of reading the pattern. Each chart division crossed has arbritrarily been assigned the value of 10 counts, readable to within about 2 counts. The pattern is read by totaling the value of the full peaks at 200 counts each, then adding the value of the beginning and ending partial peaks. The advantage of this type of readout over the conventional pipping is that extremely high count rates may be recorded. Count rates as high as 60,000 per minute are possible. High count rates, however, require high chart speeds, since, if more than 8000 counts are recorded per inch of chart, the pattern lines run together. A second advantage to this type of readout is that negative counts may be distinguished from positive counts, since the recorder pen reverses motion the instant it passes across the base line, provided the reversal does not take place at a pattern peak.

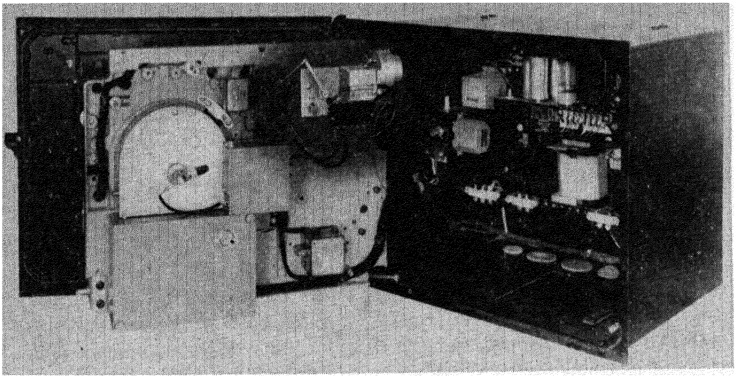

FIG. 1. Disc integrator on a standard recorder.

A third advantage is the fact that the area under any portion of the curve can be obtained by projecting down onto the pattern. This makes it possible to obtain the area under unresolved peaks and to make corrections for base line drift. The main disadvantage to this type of readout is the chance of making an error in counting the pattern peaks and in estimating the value of the partial peaks.

PERFORMANCE

Performance checks were made on two stock integrators. Each integrator was tested as installed on the same recorder.

Linearity

Table I shows the linearity as compared with the recorder chart. The recorder pen was set manually on each chart graduation to within about one-quarter of a pen line (approximately 0.005 inch or 0.05% full-scale). It will be noted that both integrators checked within a ±0.1 % deviation from the linear, except No. 129, which had a −0.3% deviation at the top end of the scale.

Repeatability

The two sets of identical peaks shown in Fig. 4 were made mechanically rather than with the aid of the recorder servo system. It will be noted that the counts are identical within the reading error, except for two of the peaks. It is not known whether the difference is due to a difference in actual area of the peaks or an error in the computing system. The difference in

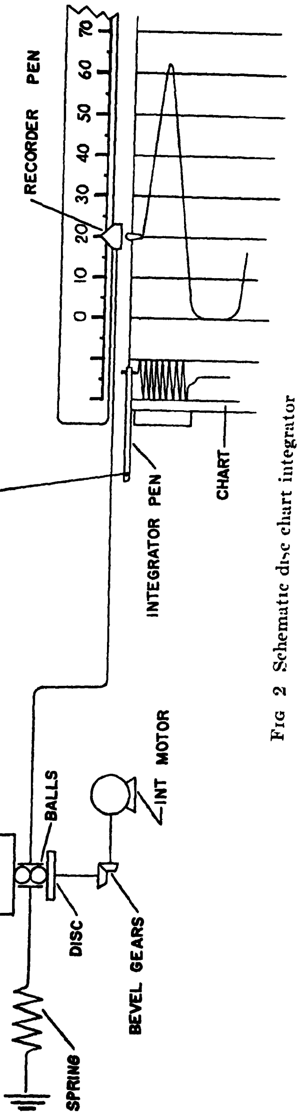

FIG 2 Schematic disc chart integrator

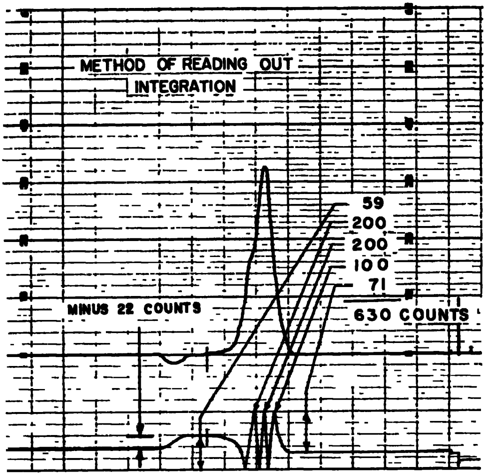

Fig. 3. Method of reading out integration

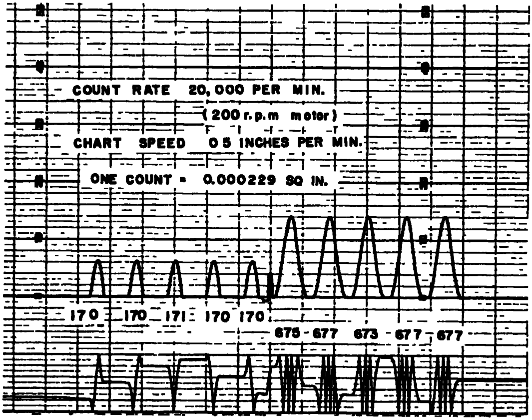

Fig. 4. Repeatability of identical peaks.

counts, however, is negligible, since one count calculates to be about 0.00046 square inches of chart area at the count rate and chart speed used.

Response

Figure 5 shows a response check. Here, in order to amplify any possible lag between the recorder pen and the integrator pen, a count rate about

TABLE I

Linearity Check

Run no.	Input		Output		
	Recorder pen setting in % full-scale	Integrator motor revolutions	Counts	%	Deviation from linear
Integrator No. 129 (stamped on case)					
1	0	100	14	0.14	+0.07
2	1	100	72	0.72	−0.07
3	10	100	992	9.92	+0.10
4	20	100	1984	19.84	−0.02
5	40	100	3998	39 98	+0.05
6	60	100	6014	60.14	+0.13
7	80	100	8012	80.12	+0.04
8	100	100	9986	99.86	−0.29
Repeat Run					
9	0	100	−10	−0.10	+0.07
10	1	100	70	0.70	−0.09
11	10	100	985	9.85	+0.03
12	20	100	1984	19 84	−0.02
13	40	100	3998	39.98	+0.05
14	60	100	6010	60.10	+0.09
15	80	100	8012	80.12	+0.04
16	100	100	9988	99.88	−0.29
Integrator No. 13					
1	0	100	−8	−0.08	+0.10
2	1	100	82	0.82	0.00
3	10	100	982	9.82	−0.05
4	20	100	1988	19.88	−0.06
5	40	100	3998	39.98	−0.08
6	60	100	6022	60 22	+0.03
7	80	100	8044	80.44	+0.12
8	100	100	10032	100.32	−0.12
Repeat Run					
9	0	100	−6	−0.06	+0.13
10	1	100	74	0 82	0.00
11	10	100	991	9.91	+0.03
12	20	100	1998	19.98	−0 06
13	40	100	4000	40.00	−0.06
14	60	100	6020	60.20	+0.01
15	80	100	8044	80.44	+0.12
16	100	100	10038	100.38	−0.06

Note: Disc Integrators Nos. 129 and 13 as mounted on a Bristol Recorder.

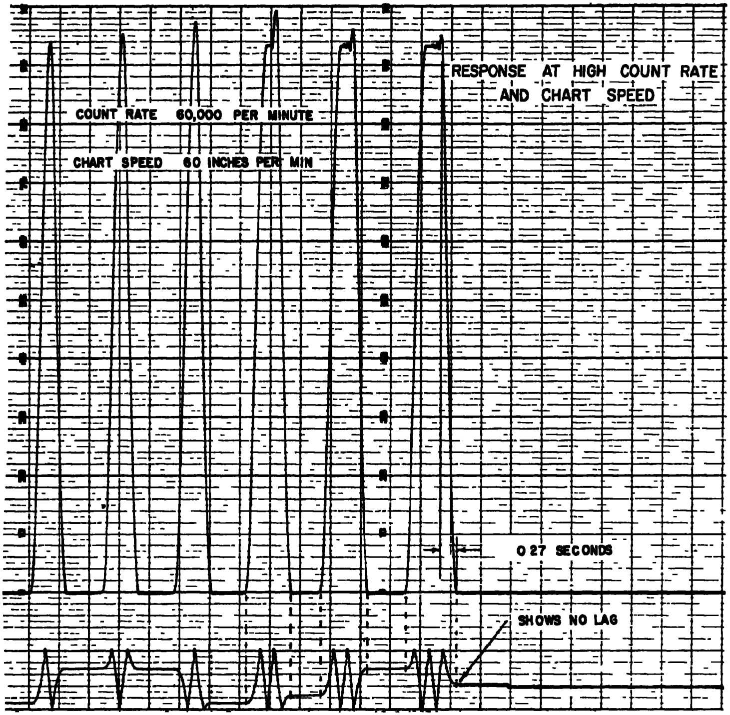

FIG 5 Response at high count rate and chart speed

six to ten times the normal was used (60,000 counts per minute) Also a recorder pen speed about double the normal was used (full-scale in 0 4 seconds). The chart shows no detectable lag at these amplified conditions, which indicates that the lag would be negligible at the normal count rates and recorder pen speeds.

APPLICATION

Figure 6 shows a chromatogram with the area counts indicated for each peak. The count rate used here was 5000 per minute full-scale, obtained with a 50-rpm integrator motor. It will be noted that the chart speed used was too slow for easy reading. A higher chart speed would have spread out the pattern. The total counts recorded for each peak would not have been affected. The optimum counts that can be easily read per inch of chart is

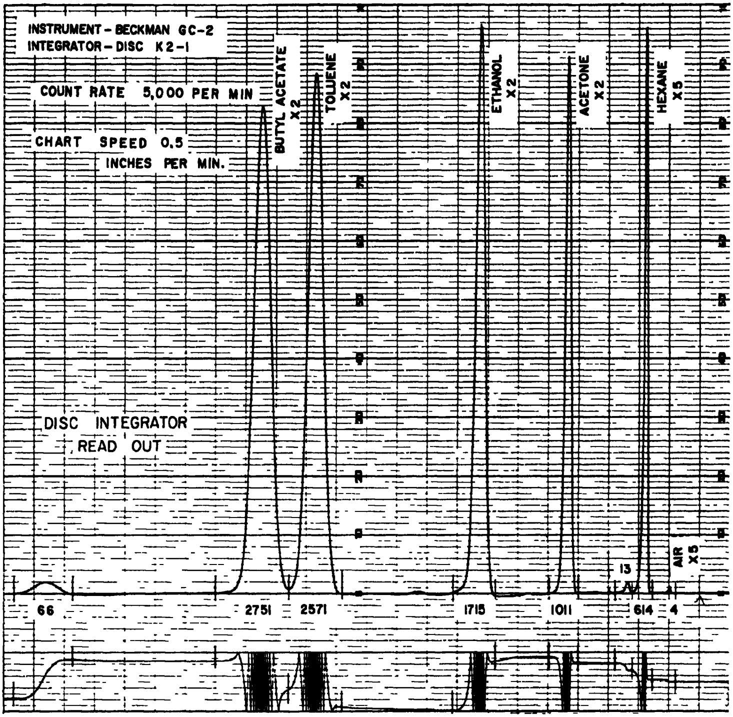

FIG 6. Disc integrator readout

about 6000 At 10,000 counts per inch of chart, the pattern can still be read, but the chance for error is high because of the close spacing of the pattern lines. It is usually necessary to experiment in order to get the best compromise between chart speed and count rate for any one application. To change the count rate range, a motor of a different rpm is installed in the integrator.

CHAPTER XIV

The Effects of Temperature, Pressure, and Type of Carrier Gas on The Sensitivity of a Thermal Conductivity Detector

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Thermal conductivity detectors are widely used in gas chromatography and because of their inherent simplicity and robustness it is probable that they will continue to be popular for some considerable time, even though much more sensitive detectors are now available. The sensitivity of a thermal conductivity cell to changes in gas composition depends on a number of factors; apart from the variables associated with the electrical network, the most important of these are operating temperature, pressure, and type of carrier gas used. The purpose of this paper is to show that a useful gain in sensitivity may be achieved by a proper choice of these variables which are also governed to some extent by the chromatographic column.

This investigation was carried out during the course of some work on the determination of minor impurities in ethylene; it had been found that a column packed with a molecular sieve (calcium aluminium silicate) gave a good separation of the impurities, and it was required to establish operating conditions which gave maximum sensitivity.

DISCUSSION

Effect of Carrier Gas

The difference in temperature between the hot wire (at t_1 °C) and the body of the thermal conductivity cell (at t_0 °C) is inversely proportional to the thermal conductivity K_1 of the carrier gas:

$$t_1 - t_0 = \frac{a}{K_1}$$

where a depends on bridge current. When the maximum bridge current is limited by the supply voltage, as in the case of a battery-driven bridge circuit, the bridge will be operated at the maximum obtainable current to give the highest sensitivity, so that a is approximately constant. Then if x is the concentration of organic vapor (of thermal conductivity K_2) the sensitivity of the detector is proportional to

$$\frac{dt}{dx} = -\frac{a}{K_1^2}\frac{dK}{dx} = -\frac{a(K_1 - K_2)}{K_1^2} \quad \text{approximately,}$$

when x is small, so that the sensitivity should be directly proportional to the difference in thermal conductivity and inversely proportional to the square of the thermal conductivity of the carrier. It follows that the carrier gas with the lowest thermal conductivity should give the greatest sensitivity, and this was confirmed by experiment, using helium (thermal conductivity 13:9 kiloergs/cm²/sec/°C) and argon (1:58 kiloergs/cm²/sec/°C) as carriers. Some measurements were also made with carbon tetrafluoride, chlorodifluoromethane, and sulfur hexafluoride as examples of gases with even lower themal conductivities, but these were not completely successful because the molecular sieve column absorbed these gases to such an extent that the test mixture was not completely resolved. The results obtained with chlorodifluoromethane, although incomplete, nevertheless showed that a very large increase in sensitivity might be obtained with these carrier gases, and this was confirmed in further experiments using a partition column in place of the molecular sieve.

Effect of Temperature

The thermal conductivities of all gases increase with temperature but the rate of increase is least for monatomic gases. It can therefore be predicted that the sensitivity of the detector should increase with temperature when the carrier is a monatomic gas of low thermal conductivity such as argon, but that it should decrease with temperature when the carrier is helium.

The Griffin V.P C. Apparatus, with which this work was done, is so designed that the column and the thermal conductivity cells are maintained at the same temperature. Thus there is an additional effect of temperature, in this case resulting from the decreased retention times at higher temperatures; however, as the temperature is raised still further the resolution eventually suffers. It is probable that a modification of the apparatus which would permit the detector to be heated independently of the column would be advantageous in many cases.

Measurements of the response of the detector to nitrogen, methane, ethane, and propane were made with argon carrier over the temperature range 80°–160°C. The results showed that the response to nitrogen and methane was almost independent of temperature, but the response to ethane and propane at 140°C was more than double the response at 80°C. In the case of propane the response apparently decreased at temperatures above 150°C but this was largely due to a falling-off in resolution.

Effect of Pressure

The thermal conductivity of an ideal gas is independent of pressure, so that on this count alone the effect of pressure on the sensitivity of a thermal conductivity detector should be small. When the detector is being used to measure small quantities of impurities, however, as in the present case, a reduction in pressure may be advantageous, since it is equivalent to reducing the volume of the detector. Measurements of the response to methane, ethane, and propane were made at various pressures from atmospheric down to 100 mm with three carrier gases; with argon and helium carriers the response was almost independent of pressure, showing that the volume of the detector was small enough to have no adverse effect, but with chlorodifluoromethane as carrier there was a small but significant increase in sensitivity at the lower pressures. The reason for this was not discovered.

Minimum Detectable Concentrations

An increased response is of no value if the noise level is increased in proportion, for the same effect could be achieved by straightforward amplification of the detector output. In order to show that the increase in sensitivity achieved by the use of a carrier gas of low thermal conductivity and by operating at an elevated temperature is a real one, the minimum detectable concentrations of methane, ethane, and propane in a 5-ml sample of gas were determined by diluting the reference mixture until the relevant peaks diminished in height to twice the average noise level, i.e., to $^1/_{100}$ of the full-scale deflection of the recorder. The minimum detectable concentrations of methane and ethane with argon carrier were respectively one-third and one-half of the lower limits with helium, the improvement was much less for propane.

Conclusions

With a thermal conductivity detector, a useful gain in sensitivity may be achieved by selecting as carrier a gas of low thermal conductivity and by operating at as high a temperature as is consistent with the required separation.

EXPERIMENTAL

Apparatus

The measurements were made in a Griffin Mk.IIA V.P.C. Apparatus (Griffin & George, Ltd., Wembley, Middlesex). In this instrument the column and the thermal conductivity cell are maintained at the same temperature.

Standard Gas Mixture

As a reference mixture to provide a large number of samples of constant composition, 30 ft^3 of slightly impure ethylene was stored in a large cylinder.

The composition of this gas had been carefully determined in the course of other work, and was known to be as follows: C_2H_4, 96.25 ± 0.02%; N_2, 0.20 ± 0.01%; CH_4, 0.05 ± 0.006%; C_2H_6, 1.30 ± 0.03%; C_3H_8, 2.20 ± 0.02%; other impurities, less than 0.05%.

Effect of Carrier Gas on Sensitivity

The column was 93 cm long × 7 mm bore and was packed with Linde molecular sieves type 13 (British Drug Houses Ltd., Poole, Dorset) graded

TABLE I

RELATIVE SENSITIVITIES WITH VARIOUS CARRIER GASES[a]

Carrier gas	Peak height in in./ml pure component		
	CH_4	C_2H_6	C_3H_8
Helium	116	98	25
Argon	311	190	28
Carbon tetrafluoride	Incomplete resolution	Incomplete resolution	Incomplete resolution
Chlorodifluoromethane	—	562	272
Sulfur hexafluoride	No resolution	No resolution	No resolution

[a] Molecular sieve column at 148°C.

TABLE II

RELATIVE SENSITIVITY TO PROPANE WITH VARIOUS CARRIER GASES[a]

Carrier gas	Peak height in in./ml C_3H_8
Argon	47
Carbon tetrafluoride	76
Sulfur hexafluoride	102

[a] Apiezon oil column at 20°C.

TABLE III

RELATIVE SENSITIVITIES AT VARIOUS TEMPERATURES[a]

Temperature, °C	Peak height in in./ml pure component			
	N_2	CH_4	C_2H_6	C_3H_8
80	200	380	76	—
102	217	366	81	16.5
120	169	339	104	22
140	180	338	158	40
160	184	300	201	28

[a] Using 93-cm molecular sieve column and argon carrier gas.

between 72–100 B.S. mesh. The reference mixture was completely resolved on this column at 148°C with argon as carrier at a flow rate of 4 liters per hour and the column outlet at atmospheric pressure.

With each carrier gas the bridge current used was the maximum obtainable from the 6-volt accumulator provided in the instrument. Analyses were carried out with each carrier using samples of the reference mixture ranging from 0.2 to 5.0 ml, and the heights of the peaks corresponding to methane, ethane, and propane were plotted against sample volume. The peak heights corresponding to unit volumes of the pure components were calculated, and the results are given in Table I.

TABLE IV

RELATIVE SENSITIVITIES AT VARIOUS PRESSURES[a]

Carrier gas	Outlet pressure, mm Hg	Peak heights in in /ml pure component			
		N_2[b]	CH_4[b]	C_2H_6	C_3H_8
Argon	760	182	315	192	29
	415	179	310	190	31
	348	154	312	191	33
	105	131	300	189	36
Helium	760	—	116	95	24
	390	—	114	80	22
	108	—	115	65	20
Chlorodifluoromethane	760	—	—	560	275
	616	—	—	654	280
	229	—	—	905	285
	21	—	—	1150	300

[a] Molecular sieve column at 150°C.

[b] Nitrogen and methane were not resolved under these conditions with chlorodifluoromethane as carrier

TABLE V

MINIMUM DETECTABLE CONCENTRATIONS[a]

Impurity gas	Carrier	
	Helium	Argon
Methane	195 ppm	65 ppm
Ethane	200 ppm	100 ppm
Propane	500 ppm	400 ppm

[a] Concentration of gas required to give a peak of 1/100 full-scale from a sample of 5 ml.

Since the reference mixture was not completely resolved on a molecular sieve column with carbon tetrafluoride and sulfur hexafluoride as carriers, the experiments were repeated using a column 400 cm long × 7 mm bore, packed with Chromosorb (Johns-Manville Co., Ltd., London) graded 52–72 B.S. mesh and impregnated with Apiezon Oil B (10% by weight). At 20°C this column resolved the reference mixture into three fractions consisting of nitrogen + methane; ethane + ethylene; and pure propane, respectively; the degree of resolution was independent of the carrier gas.

Samples ranging from 1 0 to 5.0 ml were injected and the peak heights corresponding to unit volume of propane were calculated, with the results as shown in Table II.

Effect of Temperature on Sensitivity

Using the 93-cm molecular sieve column described above and argon carrier gas, the relative sensitivities for nitrogen, methane, ethane, and propane were determined at various temperatures in the range 80°–160°C. The results are summarized in Table III.

Effect of Pressure on Sensitivity

Using the 93-cm molecular sieve column at 150°C, the relative sensitivities for nitrogen, methane, ethane, and propane were determined at various column outlet pressures with three different carrier gases; in these experiments the pressure drop across the column was maintained at a constant value, and hence the flow rate was approximately constant. The results are given in Table IV.

Minimum Detectable Concentrations

The minimum detectable concentration of each impurity was determined by diluting the reference mixture with carrier gas until the peak obtained from a 5-ml sample of gas was less than 0.1 in. (i.e., 1/100 full-scale) in height. This corresponded to a signal-to-noise ratio of approximately 2:1. These measurements were made on the molecular sieve column at 160°C with argon and helium carriers; the results are given in Table V.

CHAPTER XV

Determinations of C_1 through C_7 Hydrocarbons in a Single Run by a Four-Stage Gas Chromatograph

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INTRODUCTION

Refinery, pilot plant, and research activities in the petroleum industry require detailed analyses of hydrocarbon gases and light liquids. Samples with relatively narrow boiling ranges and limited types of components can be dealt with satisfactorily by conventional methods. But the usual methods are too costly and slow for routine use, and cannot completely determine all the unsaturates that may be present.

Gas chromatographic methods for routine use have been reported for less complex mixtures and less complete analyses. More elaborate methods have been proposed but these are better suited to special problems rather than to routine operation by non-technical personnel. This is due to the many conflicts that invariably occur, especially between members of different homologous series.

Generally speaking, partitioning liquids are more satisfactory for isothermal separations involving a wide range of compounds than adsorbents. Keulemans *et al.* (*1*) found that dimethylformamide (DMF) on crushed brick at 0°C very effectively separated all the butanes and butenes, but that propylene and isobutane coincided. They suggested the use of a nonpolar column in front of the DMF column in order to resolve this conflict.

Our original efforts to separate C_1 through C_5 hydrocarbons in this way were unsuccessful because other separations deteriorated as the propylene-isobutane split improved. Polar compounds that gave similar but complementary peak spacings proved better for this purpose. Diethylbenzoate initially was found to be a satisfactory modifier for the DMF. Performance of this column, previously described briefly (*2*), is recorded in Table I and Fig. 1. C_1–C_6 saturates, C_2–C_4 monolefins, air, CO_2, and acetylene are separated adequately except for conflicts between cyclopropane and neopentane, and 2,3-dimethylbutane and 2-methylpentane. However, this partitioning mixture is relatively volatile and must be replenished by redeposition from solvent after about 40 hours' service.

For simplified routine use, a substantially nonvolatile partitioning liquid

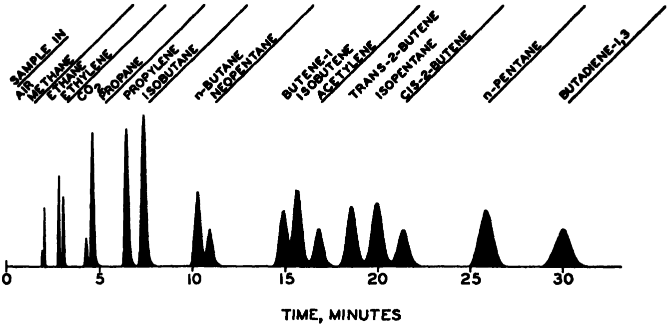

FIG. 1. Separations with 30 ft of a 23v:77v ethyl benzoate:dimethylformamide column at 78°F (30 psig helium → 120 cc/min NTP).

with similar separating characteristics was sought. Fredericks and Brooks (*3*) report peak spacings similar to DMF's with dimethylsulfolane. Therefore, similar compounds having minimum viscosity, vapor pressure, and molecular weight, combined with maximum polarity, solubility for hydrocarbons, and density (*4*), were screened separately and in complementary combinations. Three parts of *n*-propyl sulfone modified by about one part of dimethylsulfolane (PS:DMS) best met the prime requirements of favorable peak spacings and low volatility. However, the loss in selectivity accompanying the higher average molecular weight and viscosity of this mixture requires a 50 % longer column for generally comparable separations. A chromatogram with 50 ft of this column packing is shown in Fig. 2, and retention data for 82 compounds are listed in Table II.

Elution of $C_5^=$–C_7's from this 50-ft column takes much too long, sensitivity is lost because of peak broadening, and numerous conflicts occur among the different homologous series. The conflict between cyclopentane and *n*-hexane is particularly objectionable. In order to shorten the elution time for the slower compounds, and to resolve and rearrange the many conflicts among them, the present four-stage gas chromatograph was constructed. This system processes different portions of a single sample entry by multiple flow routing plus simultaneous multiple detection.

Simmons and Snyder (*5*) used a Pelletex (*6*) column for preliminary separations in order of carbon atoms per molecule. They routed fractions containing one carbon-number at a time into a silicone oil column for further separation. Although dual flow routing was employed, they used only one detector. They did suggest, however, that multistage use of a primary nonpolar column and two or more parallel polar secondary columns would achieve the "ultimate in separation."

TABLE I

RELATIVE RETENTIONS AT 78°F FOR A 23v:77v ETHYLBENZOATE: DIMETHYLFORMAMIDE[a] COLUMN IN ORDER OF APPEARANCE

Peak No.	Compound	Retention ratio	Peak No.	Compound	Retention ratio
1	Hydrogen, air, etc.	0.082	25	1-Pentene	1.71
2	Methane	0.087	26	*cis*-2-Pentene	1.81
3	Ethane	0.118	27	2,3-Dimethylbutane	1.87
4	Ethylene	0.125	28	2-Methylpentane	1.89
5	Carbon dioxide	0.173	29	2-Methyl-2-butene	2.06
6	Propane	0.188	30	2-Methyl-1,3-butadiene	2.18
7	Propylene	0.261	31	3-Methylpentane	2.20
8	Isobutane	0.298	32	3-Methyl-1-pentene	2.28
9	*n*-Butane	0.41	33	Cyclopentane	2.38
10	2,2-Dimethylpropane	0.43	34	2,3-Dimethyl-1-butene	2.58
11	Cyclopropane	0.43	35	*n*-Hexane	2.59
12	1-Butene	0.58	36	*trans*-4-Methyl-2-pentene	2.63
13	Isobutene	0.61	37	1,2-Pentadiene	2.94
14	Acetylene	0.64	38	Cyclopentene	3.22
15	*trans*-2-Butene	0.72	39	1-Hexene	3.35
16	Isopentane	0.78	40	*n*-Heptane	3.68
17	*cis*-2-Butene	0.83	41	2-Methyl-1-pentene	3.91
18	3-Methyl-1-butene	1.00	42	2-Methyl-2-pentene	3.94
19	*n*-Pentane[b]	1.00	43	Methylcyclopentane	4.08
20	1,3-Butadiene	1.12	44	*trans*-3-Methyl-2-pentene	4.08
21	2,2-Dimethylbutane	1.36	45	*cis*-2-Hexene	4.12
22	3,3-Dimethyl-1-butene	1.42	46	*cis*-2-Methyl-2-pentene	4.5
23	2-Methyl-1-butene	1.62	47	Cyclohexane	5.6
24	*trans*-2-Pentene	1.68	48	2-Ethyl-1-butene	8.7
			49	Cyclohexene	9.1
			50	Benzene	19

[a] Forty grams of (23v:77v ethyl benzoate: dimethylformamide) deposited from 2 vols. of ether per 100 grams of 30–80 mesh C-22 brick. Rewetting is required after 10 to 20 SCF of carrier gas have passed through (40–80 hr).

[b] Typical time for n-C_5 through a 30-ft column is 25 minutes, and 5300 theoretical GC plates are developed, using 30 psig helium (120 cc/min NTP).

Davis and Schreiber (*7*), Madison (*8*), and Taylor and Poli (*9*) have described two-stage gas chromatographs with two columns, detectors, and recording systems in series for analyzing fixed gases (*10*) as well as hydrocarbons. The Taylor and Poli system is marketed by Fisher Scientific as

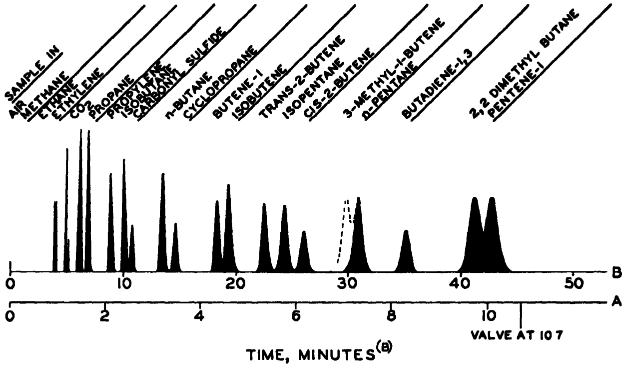

FIG 2. Separations with 50 ft of a 3:1 *n*-propyl sulfone:dimethylsulfolane column at 78°F (30 psig helium → 85 cc/min NTP). Time scales for A and B detectors superimposed on chromatogram

their Gas Partitioner. Guild and Bingham (*11*) have described the Burrell Corporation's Model K-5 Kromo-Tog as a dual gas chromatograph that can be used as two stages in series. Hurn *et al.* reported two-, three- (*12*, *13*), and four-stage (*14*) gas chromatographic systems for analysis of automotive exhaust gases, using various column temperatures. The Hurn systems resolved many compounds and were extraordinarily effective, but did not separate 1-butene and isobutene, etc.

Dietz (*15*) reported the use of two complete gas chromatographs in series to separate the light ends of full-range cracked naphthas while estimating the proportion of heavier material that was diverted from the second unit. Brenner, O'Brien, and Coates (*16*) described a three-stage apparatus marketed by Perkin-Elmer as Model 188 Vapor Fractometer. This instrument contains three independent gas chromatographs and recording systems, interconnected by two flow routing valves, with needle valves for flow balancing. It was designed for analysis of gasolines and other wide boiling mixtures that can be adequately resolved with three stages.

The present system provides a complete analysis of a single sample entry for C_1–C_7 paraffins, 7 common cycloparaffins, C_2–C_6 unsaturates, and 7 individual inorganic gases. It is operated routinely by nontechnical personnel, usually requires about 1¼ hours of instrument time per sample, and has relatively few conflicts.

EXPERIMENTAL

Apparatus and Procedure

Our analytical needs called for at least four columns and detection points. The columns are described in Table III. Provision was made to divert the

TABLE II

Relative Retentions at 78°F for a 73 wt. 27 wt *n*-Propylsulfone·2,4-Dimethylsulfolane[a] Column in Order of Appearance

Peak No.	Compound	Retention ratio	Peak No.	Compound	Retention ratio
1	Fixed gases	0.121	41	*n*-Hexane	2.46
2	Methane	0.125	42	*trans*-4-Methyl-2-pentene	2.60
3	Ethane	0.155	43	*cis*-4-Methyl-2-pentene	2.60
4	Ethylene	0.162	44	2,3-Dimethyl-1-butene	2.78
5	Carbon dioxide	0.204	45	2,2-Dimethylpentane	2.92
6	Propane	0.227	46	2-Methyl-1,3-butadiene	3.03
7	Propylene	0.291	47	2,4-Dimethylpentane	3.11
8	Isobutane	0.327	48	3-Methyl-1,2-butadiene	3.14
9	Carbonyl sulfide	0.347	49	Cyclopentene	3.19
10	*n*-Butane	0.44	50	1-Hexene	3.43
11	Acetylene	0.45	51	2,2,3-Trimethylbutane	3.49
12	2,2-Dimethylpropane	0.45	52	2-Methyl-1-pentene	3.54
13	Cyclopropane	0.48	53	1,2-Pentadiene	3.57
14	1-Butene	0.59	54	*trans*-3-Hexene	3.60
15	Isobutene	0.62	55	2,3-Pentadiene	3.65
16	Hydrogen Sulfide	0.62	56	*cis*-3-Hexene	3.70
17	Propadiene	0.62	57	1-*trans*-3-Pentadiene	3.83
18	*trans*-2-Butene	0.73	58	*trans*-2-Hexene	3.89
19	Isopentane	0.79	59	Methylcyclopentane	3.92
20	*cis*-2-Butene	0.84	60	2-Ethyl-1-butene	4.0
21	3-Methyl-1-butene	0.97	61	2-Butyne	4.1
22	*n*-Pentane[b]	1.00	62	2-Methyl-2-pentene	4.2
23	1,3-Butadiene	1.12	63	3,3-Dimethylpentane	4.2
24	Propyne	1.13	64	*cis*-2-Hexene	4.3
25	2,2-Dimethylbutane	1.33	65	1-*cis*-3-Pentadiene	4.3
26	1-Pentene	1.38	66	1,5-Hexadiene	4.4
27	3,3-Dimethyl-1-butene	1.54	67	2-Methylhexane	4.4
			68	2,3-Dimethylpentane	4.9
28	2-Methyl-1-butene	1.57	69	3-Methylhexane	5.0
29	1,2-Butadiene	1.62	70	1,3-Cyclopentadiene	5.3
30	*trans*-2-Pentene	1.62			
			71	2,3-Dimethyl-2-butene	5.5
31	*cis*-2-Pentene	1.79	72	Cyclohexane	5.5
32	1,4-Pentadiene	1.79	73	3-Ethylpentane	5.5
33	2,3-Dimethylbutane	1.84	74	1,1-Dimethylcyclopentane	5.7
34	2-Methylpentane	1.84			
35	2-Methyl-2-butene	2.03	75	1-*trans*-3-Dimethylcyclopentane	6.1
36	3-Methylpentane	2.11			
37	1-Butyne	2.35	76	*n*-Heptane	6.2
38	Cyclopentane	2.38	77	1-Methylcyclopentene	7.6
39	3-Methyl-1-pentene	2.43	78	Methylcyclohexane	9.5
40	4-Methyl-1-pentene	2.43	79	Cyclohexene	9.7
			80	Benzene	30
			81	Toluene	80
			82	Xylenes	200

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[a] Thirty-five grams of (73% wt *n*-propylsulfone + 27% wt 2,4-dimethylsulfolane) deposited from solvent per 100 grams of 30–80 mesh Chromosorb.

[b] Typical time for *n*-pentane through a 50-ft column is 35 minutes, and the theoretical GC plates are 7500, using 30 psig inlet helium (85 cc/min NTP).

TABLE III

FOUR-STAGE GAS CHROMATOGRAPHY COLUMNS[a]

Column	Nature	Active agent	Length, ft
A	Polar	3-*n*-Propylsulfone[b] 1-Dimethylsulfolane	10
B	Polar	3-*n*-Propylsulfone[b] 1-Dimethylsulfolane	30
C	Adsorbent	Linde-type #13X Molecular Sieve 14–30 mesh	12
D	Nonpolar	*n*-Hexadecane[b]	2½

[a] ¼-in. OD copper tubing used.

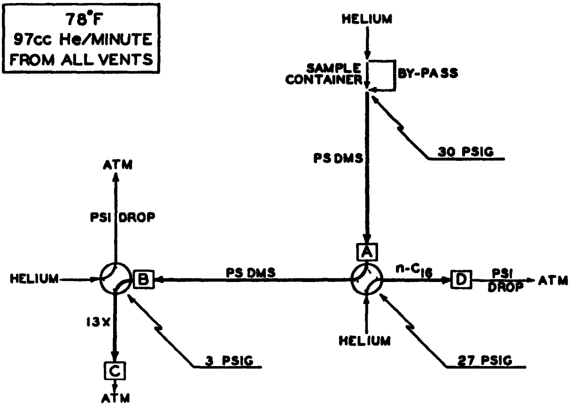
[b] 35% wt of 35–80 mesh Chromosorb.

more slowly eluted peaks after they had passed through one quarter of the PS:DMS column into a nonpolar *n*-hexadecane (*17*) column to separate or at least rearrange conflicting compounds. Meanwhile, the earlier peaks could be eluted through the rest of the PS:DMS column, with the methane and fixed gases continuing through an additional adsorption column.

The Chromosorb supporting solid should be freed of fines to minimize pressure drop. We agitate 35–80 mesh Chromosorb with diethylether and quickly decant off the suspended fines. The partition columns are prepared by folding ¼ inch OD copper tubing into a U-shape and gravity-filling both arms with the Chromosorb. The column is vibrated during introduction of solid, then plugged with glass wool and coiled to a convenient over-all size.

The partitioning liquid is diluted with three volumes of diethylether and forced through the column (*2*). Roughly 10 cc of solution and 1 psi of inert gas pressure (e.g., N_2) are required for each foot of column length. Gas flow is continued until the odor of ether disappears, usually overnight for a 50-ft column. We apply partitioning liquid equal to 34 ± 2 % of the weight of solid in the column as determined by weighing the column during preparation. More or less ether may be used to control the deposited weight. Previously wetted columns can be rewetted in the same way, because the fresh solution removes the prior liquid. Applying the PS:DMS without solvent (*18*) reduces optimum liquid loading to about 25 % and decreases the separation between air and methane, and ethane and ethylene. Batch-to-batch differences in composition of commercially available *n*-propylsulfone and dimethylsulfolane have been encountered. We have had to vary the proportion of *n*-propylsulfone from 73 to 77 % wt to center isopentane between *cis*- and *trans*-2-butene in the resulting chromatogram.

The flow system and operating cycle of the four-stage gas chromatograph are shown in Fig. 3. Detectors are located at the exits of each of the four columns, as indicated by the letters A, B, C, and D. The flow-routing



Operating Cycle

Time, min	Event	Flow routing	Detectors recording
0.0	Enter sample	He → A → B → C	B & C (& D)
5.4	C_2^- past B	A → B → Dummy He → C	B & C (& D)
10	CO out of C	A → B → Dummy He → C	A & B (& D)
10.7	1-C_5^- past A	A → D → Dummy He → B → Dummy	A & B & D
70 (−100)	End of run	Reset	Reset

Fig. 3 Flow diagram for the four-stage gas chromatograph.

valves are shown as four-way glass stopcocks which must be secured against pressure blowout with suitable spring clamps. We lubricate every 2 weeks with Celvacene medium stopcock grease. With a little ingenuity greaseless valves, such as the Perkin-Elmer 6-port gas sampling valve, or toggle or solenoid valves, may be used.

We have been able to satisfactorily balance the various pressure drops only by using actual dummy columns. The length of unwetted Chromosorb in ¼ inch OD copper tubing is adjusted by trial and error so that the alternate routes offer equal flow resistance. Helium is supplied to the system at 30, 27, and 3 psig from low-range gas pressure regulators to maintain a flow of 97 cc/min. NTP throughout the system. Pressure fluctuations are suitably dampened by the A, B, and D columns. A packed column with about 7-psig drop is placed between the regulator and flow routing valve before column C. A separate helium stream from the 30-psig regulator is piped through fixed flow resistances to permit about 30 cc/min NTP to flow past all four reference thermistors in series before venting to the atmosphere. The helium flows from all four vents are brought to one location for metering by a soap bubble flowmeter. During nonuse periods these lines are capped and the entire system is kept under slight helium pressure. The brief disturbances due to valve changes occur at cycle times that do not interfere with peak height measurements.

The detection system consists of four independent thermistor bridges, all utilizing matched pairs of Fenwall G-112 thermistors (8000 ohms at 77°F). We prefer to mount the measuring thermistors directly in the flow path and to keep them energized continuously. The volumes between the ends of the columns and the thermistors are less than 1 cc. The bridges in the A and B detection systems contain 400-ohm fixed resistances and utilize Perkin-Elmer 3200-ohm stepped attenuators to keep the recorders on scale. Fixed resistances of 1000 ohms are used in the C and D bridges to limit sensitivity and the zero adjustment resistance is located in series with the reference thermistor in these cases. The C and D bridges also use the Perkin-Elmer attenuators plus a fixed $\frac{1}{10}$ attenuator on the C output signal to keep 100% methane peaks on scale. Detector signals, after attenuation, are fed to recording potentiometers which in our case are as shown in Table IV.

Thus, three recording pens serve the four bridges. The Wheelco recorder charts the C record for the first 9 minutes, and is then switched over to record the A signal for the balance of the run. It is equipped with Wheelco's electronic Model B-2 Integrator (*19*), which has a pipping pen readout. Maximum pipping rate is 3270 pips/min or 6540 pips/inch of chart travel, and every tenth and hundredth pips stands out. This recorder is also used to standardize all four bridge voltages via a 0.0001 voltage divider. The voltage supplies to A, C, and D bridges are set individually to 9.00 volts,

TABLE IV

Detector bridge	Recorder[a]				
	Designation	Pen color	Full span pen response, sec	Range, mv	Chart speed, inches/min
A	Wheelco, with integrator	Red	2	1	½
C	Wheelco, with integrator	Red	2	1	½
B	L & N, 2 pen	Red	1	10	1
D	L & N, 2 pen	Green	1	1	1

[a] All recorder pens operate a buzzer when they reach 90% of full scale to alert the operator for possible attenuation.

TABLE V

Column	Peak sharpness[a]	Theoretical plates[b]
A	15	1300
B	31	5600
C	27	4200
D	22	2800

[a] Peak sharpness = retention/half-width [see reference (*4*)].

[b] Theoretical GC plates = $(\text{retention/projected base})^2 \times 16$ [see reference (*21*)] = $5.8\ (\text{peak sharpness})^2$ (see discussion)

and the B bridge is set to 8.00 volts, from 12-volt storage batteries in series with suitable 10-turn helipots.

In order to enter samples as sharply as possible into the A column, a streamlined glass system was originally used. More recently we constructed a toggle valve sampler similar to that described by Dimbat, Porter, and Stross (*20*). We use ⅛-inch Hoke helium-leak-tested, stainless steel toggle valves with neoprene seats. Nylon inserts minimize dead space. The normal chromatographic sample size is 27 cc at 100 or 400 mm Hg absolute. Larger samples are used when analyzing for traces.

The system and its auxiliaries are used in a room thermostatically controlled at 78° ± 2°F and are insulated with glass wool surrounded by metal. Base line drift due to temperature changes does not exceed one millivolt per hour.

Relative sharpness values for median peaks are given in Table V.

The operation of the various columns can be illustrated with the help of Fig. 3. Fixed gases, methane, ethane, and ethylene are routed past the B detector to the C column. Here they are separated into H_2, O_2, N_2, CH_4, and CO. The C_2's emerge so slowly from this column as to be imperceptible. A chromatogram from the C column is shown in Fig. 4. The valve below B is rotated at 5.4 minutes, just after the ethylene and well before the CO_2 peak (see Fig. 2) on the B column, and between the oxygen and nitrogen peaks on the C column.

As soon as the CO peak has returned to the C column base line, the Wheelco recorder is switched from the C to the A detecting system (about 9 minutes from sample entry). At about 10.7 minutes (as shown by the appended time scale for the A column in Fig. 2), when the descending shoulder of the 1-pentene peak reaches base line or starts to reverse (Fig. 5), the flow-routing valve after the A detector is rotated to divert subsequent peaks into the D column. Figure 5 illustrates A vs. D readout (cyclopentane would appear as shown by the dotted line). Prior compounds continue to be eluted through the B column. The run is continued for 70 to 100 minutes from sample entry unless the A record indicates that no

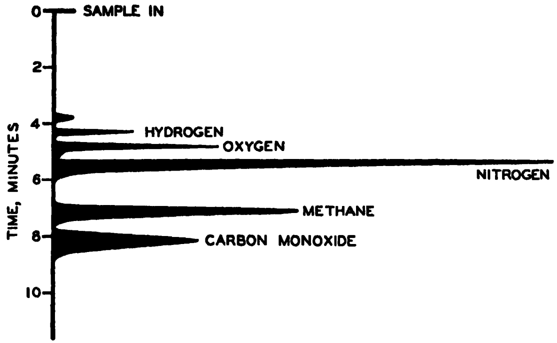
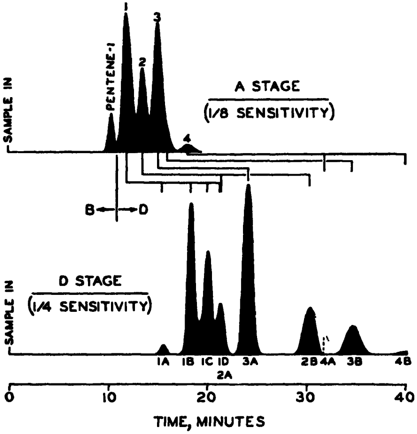


FIG. 4. Chromatogram from the C column of Fig 3.



Peak No.	Identity	Peak No.	Identity
1A	1,2-Butadiene	2B	2,3-Dimethylbutane
1B	2-Methyl-1-butene	2B	2-Methylpentane
1C	*trans*-2-Pentene	3A	2-Methyl-2-butene
1D	3,3-Dimethyl-1-butene	3B	3-Methylpentane
2A	*cis*-2-Pentene	4A	Cyclopentane
		4B	*n*-Hexane

FIG. 5. Matching chromatograms from A and D stages of Fig. 3.

peaks can be expected on D. Actually, the D record can be continued if peaks are expected (from the A record) for 15 minutes after the next sample is added, before any overlap can occur. The peaks from two successive samplings can be distinguished easily because the half-widths of the previous ones will be five times those of peaks from the very next sample, etc.

Calibrations and Calculations

Known materials are used for empirical (*2*), (*22*) qualitative and quantitative calibrations. Phillips, Matheson, and American Petroleum Institute pure compounds are used individually and in blends, and Phillips hydrocarbon mixtures also are utilized. The compounds for which calibrations were obtained are summarized in Table VI.

The complete list of compounds including retention and other calibration data is reported in Table VII, and the sensitivity data are summarized in Table VIII. (Apparent discrepancies between the number of compounds listed above and in Tables II and VII are explained by inclusion of toluene and xylenes and the omission of H_2, O_2, N_2, and CO from Table II, and by the doubling up of two pairs of hexenes in Table VII.)

The repeatability of this four-stage gas chromatograph permits the use of peak heights as the primary measure of concentrations, supplemented by half-widths only when overloading causes peak broadening. The B-stage peak heights for air, CO_2, and the C_1–C_4 paraffins and monoolefins are plotted against concentration in Fig. 6, using log scales. On the straight

TABLE VI

Molecular type	Number	Identity
Inorganic gases	8	Air, O_2, CO, H_2S[a], H_2, N_2, CO_2, COS
Paraffins	22	C_1–C_7
Cycloparaffins	7	CyC_3, CyC_5, CyC_6, Two $DiMeCyC_5$'s, $MeCyC_5$, $MeCyC_6$
Monoolefins		
Aliphatic	27	C_2–C_6
Cyclic	3	CyC_5^{-}, $1\text{-}MeCyC_5^{-}$, CyC_6^{-}
Diolefins		
Aliphatic	11	C_3–C_5, $1,5\text{-}C_6^{--}$
Cyclic	1	$1,3\text{-}CyC_5^{--}$
Acetylenes	4	C_2–C_4
Aromatics	1	Benzene
	84	

[a] Stainless steel column used.

TABLE
FOUR-STAGE GAS

No.	Compound[a]	Boiling, point, °F	Peak retention, inches[b]			
			A	B	C	D
1	Hydrogen	−423			2.2	
2	Oxygen	−297			2.5	
3	Nitrogen	−319			2.9	
4	Methane	−259			3.7	
5	Carbon monoxide	−310			4.5	
6	Air (and other fixed gases)	—	0.65	3.75		1.72
4A	Methane	−259		3.86		
7	Ethane	−128		4.8		
8	Ethylene	−155		5.0		
9	Carbon dioxide	−109		6.3		
10	Propane	−44		7.0		
11	Propylene	−54		9.0		
12	Isobutane	11		10.1		
13	Carbonyl sulfide	−54		10.7		
14	*n*-Butane	31		13.5		
15	(Acetylene)	−119		13.9		
16	(2,2-Dimethylpropane)	49		13.9		
17	Cyclopropane	27		14.7		
18	1-Butene	20.7		18.3		
19	Isobutene	19.6		19.3		
20	(Hydrogen sulfide)	−79		19		
21	(Propadiene)	−30		19.3		
22	*trans*-2-Butene	34		22.5		
23	Isopentane	82		24.3		
24	*cis*-2-Butene	39		25.9		
25	3-Methyl-1-butene	68		29.9		
26	*n*-Pentane	97		30.9		
27	1,3-Butadiene	24		34.7		
28	Propyne	−10		34.9		
29	2,2-Dimethylbutane	121		41.2		
30	1-Pentene	86	5.1	42.7		(16.8)
31	1,2-Butadiene	52	6.0	(50.4)		15.5
32	2-Methyl-1-butene	88	5.8			18.3
33	(1,4-Pentadiene)	79	6.8			18.8
34	*trans*-2-Pentene	97	6.0			20.1
35	(1-Butyne)	47	8.9			20.6
36	3,3-Dimethyl-1-butene	106	5.7			21.4
37	*cis*-2-Pentene	98	6.6			21.4
38	2-Methyl-2-butene	101	7.5			24.1
39	2-Methyl-1,3-butadiene	93	11.2			30.0

NOTE: 30 psig → Atm helium; 100 cc NTP/minute; 78°F; valved at 5.4 & 10.7

VII

CHROMATOGRAPH: DATA SUMMARY

Peak half-width, inches					Peak height per mol. %, inches						
A	B	C 100 mm	C 400 mm	D	A^c	B 100 mm	B 400 mm	C 100 mm	C 400 mm	D^c	No
		0.056	—					0.8	–		1
		0.07	0.09					12.2	34		2
		0.10	0.11					8.65	32		3
		0.15	0.16					5.6	22		4
		0.23	0.24					3.6	14		5
0.035	0.11			0.11	340	33	88			1500	6
	0.12					32	—				4A
	0.15					33	112				7
	0.17					30	105				8
	0.20					24	88				9
	0.26					24	88				10
	0.32					19	72				11
	0.41					19	72				12
	0.37					15	57				13
	0.50					16	61				14
	0.47					7.5	30				15
	0.50					13	52				16
	0.49					11	44				17
	0.67					12	48				18
	0.71					11	44				19
	--					—	—				20
	0.64					9	36				21
	0.76					10.2	41				22
	0.88					9.4	38				23
	0.86					8.7	35				24
	1.03					8.0	32				25
	1.05					8.1	32				26
	1.01					6.2	25				27
	1.05					4.7	19				28
	1.40					6.1	24				29
0.31	1.38			(0.83)	(100)	5.8	23			(60)	30
0.36				0.79	67					47	31
0.35				0.90	89					56	32
0.44				0.93	70					51	33
0.36				0.97	86					52	34
0.56				1.0	55					50	35
0.39				1.00	80					50	36
0.42				1.00	74					50	37
0.46				1.17	67					43	38
0.71				1.44	44					35	39

minutes, 27 cc sample at 100 mm Hg abs. (For footnotes, see next two pages.)

TABLE

No.	Compound[a]	Boiling point, °F	Peak retention, inches[b]			
			A	B	C	D
40	3- & 4-Methyl-1-pentene	129	9.0			30
41	2,3-Dimethylbutane	136	6.8			30.3
42	2-Methylpentane	140				
43	Cyclopentane	121	8.8			31.3
44	3-Methyl-1,2-Butadiene	104	11.6			32.5
45	*trans*- and *cis*-4-Methyl-2-pentene	137 & 133	9.6			33.8
46	3-Methylpentane	146	7.8			34.7
47	2,3-Dimethyl-1-butene	132	10.3			35.4
48	(2-Butyne)	81	15.4			35.6
49	Cyclopentene	111	11.8			35.6
50	(1,2-Pentadiene)	113	13.6			37.4
51	(2,3-Pentadiene)	119	13.9			38.6
52	(1-*trans*-3-Pentadiene)	108	14.6			39
53	*n*-Hexane	156	9.1			40
54	(1-*cis*-3-Pentadiene)	111	16 4			43
55	1-Hexene	146	12.7			44
56	2-Methyl-1-pentene	144	13.1			45
57	*trans*-3-Hexene	154	13.3			48
58	*cis*-3-Hexene	153	13.7			50
59	(1,5-Hexadiene)	139	16.7			50
60	(1,3-Cyclopentadiene)	108	20.2			51
61	2,2-Dimethylpentane	175	10.8			52
62	*trans*-2-Hexene	154	14.4			52
63	2-Ethyl-1-butene	148	14.8			52
64	2-Methyl-2-pentene	153	15.4			54
65	2,4-Dimethylpentane	177	11.5			56
66	*cis*-2-Hexene	155	15.9			56
67	Methylcyclopentane	161	14.5			57
68	2,2,3-Trimethylbutane	178	12.9			60
69	2,3-Dimethyl-2-butene	164	20 2			70
70	3,3-Dimethylpentane	187	15.5			74
71	Cyclohexane	177	20.3			81
72	2-Methylhexane	194	16.3			82
73	2,3-Dimethylpentane	194	18 0			86
74	3-Methylhexane	197	18.3			91
75	(1,1-Dimethylcyclopentane)	190	21.3			88
76	1-Methylcyclopentene	167	28			94
77	3-Ethylpentane	200	20.4			100
78	(1-*trans*-3-Dimethylcyclopentane)	197	22.5			100
79	*n*-Heptane	209	23.1			118
80	(Cyclohexene)	181	37			120
81	(Methylcyclohexane)	214	35			150
82	(Benzene)	176	109			260

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[a] Compounds in parentheses are not normally sought.

[b] Chart speeds: A & C = ½ inch per min; B & D = 1 inch per min.

[c] Multiply by 4 for 400-mm samples, except for air.

VII (*Continued*)

Peak half-width, inches					Peak height per mol. %, inches						
A	B	C		D	A[c]	B		C		D[c]	No.
		100 mm	400 mm			100 mm	400 mm	100 mm	400 mm		
0.57				1.44	54					35	40
0.48				1.50	65					33	41 42
0.51				1 46	53					31	43
0.72				1.56	43					32	44
0.60				1.62	52					31	45
0.51				1.75	61					29	46
0.65				1.70	48					29	47
0.96				1.6	32					31	48
0.75				1.67	36					27	49
0.80				1.78	39					28	50
0.82				1.85	38					27	51
0.89				1.88	35					27	52
0.60				2.06	52					24	53
0.97				2.06	32					24	54
0.77				2.06	40					24	55
0.79				2.17	39					23	56
0.80				2.35	39					21	57
0.83				2.5	37					20	58
0.98				2.4	32					21	59
1.19				2.4	23					19	60
0.75				2.9	41					17	61
0.87				2.6	36					19	62
0.89				2.6	35					19	63
0.93				2.8	33					18	64
0.72				2.8	43					18	65
0.96				2 7	32					19	66
0.91				2.8	30					16	67
0.85				2.9	36					17	68
1.20				3.2	26					16	69
1.00				3.6	31					15	70
1.27				3.8	21					12	71
1.07				4.2	29					12	72
1.12				4.3	28					12	73
1.18				4.6	26					11	74
1.33				4.2	20					11	75
1.63				3.9	17					12	76
1.29				5.0	24					10	77
1.40				4.8	19					9	78
1.45				5.5	21					9	79
2.2				5.6	12					8	80
2.2				7.0	12					6	81
—				—	[d]					[e]	82

[d] Use Peak ht × half-width/mole % = 24.

[e] Use Peak ht × half-width/mole % = 39.

TABLE VIII

SENSITIVITY RANGES ON THE FOUR-STAGE GAS CHROMATOGRAPH

Stage	Detector sensitivity			
	(mv−ml)/ mg $n-C_4$	Early and late compounds	Peak height per mole %, inches	Detection limits, mole %
A	6600	*trans*-2-Pentene	86	0.002
		n-Heptane	21	0.02
B	7900	Methane	32	0.003
		2,2-DiMeButane	5	0.01
C	3500 ÷ 10	Oxygen	12	0.01
		Carbon monoxide	3.6	0.02
D	5000	*trans*-2-Pentene	52	0.002
		MeCyclopentane	16	0.01

NOTE: Second column: Data from Dimbat, Porter, and Stross (*20*). Fourth and fifth columns: 3.6 cc vapor STP

line portion of these curves it is more convenient to use the linear slope as a divisor to calculate mole per cent arithmetically:

$$\text{mole } \% = \frac{H}{S} \tag{1}$$

where H = observed peak height, inches; and
S = linear slope of the low concentration straight line part of the calibration curve, inches of peak height per mole per cent of compound.

Quantitative data for the other peaks are expressed exclusively in terms of S, except for more than 1 % hydrogen.

Equation (1) can be modified to account for peak broadening caused by component overloading as follows:

$$\text{mole } \% = \frac{H}{S} \cdot \frac{W_1}{W_0} \tag{2}$$

where W_1 = actual half-width, inches;
W_0 = minimum (normal) half-width, inches.

Rearranging Eq. (2) to combine the invariant terms as a constant:

$$\frac{HW_1}{\text{mole } \%} = SW_0 = K_{x,y} \tag{3}$$

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[1] D-delay = [(Compd -Air)$_D$-2(Compd.-Air)$_A$], Minutes, where the subscripts refer to the retentions posted for the A and D stages in Table VII.

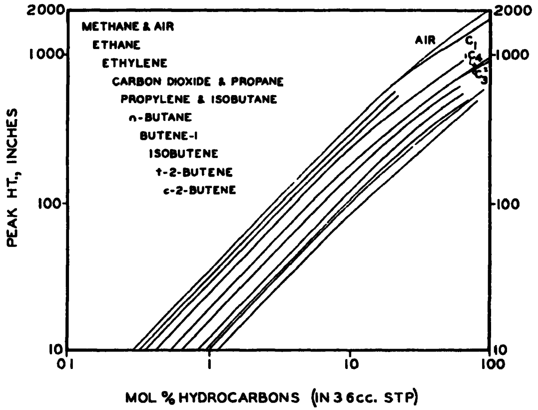

FIG 6. Quantitative calibration curves for the early compounds from the B column of Fig 3

where $K_{x,y}$ = a constant, inches²/mole %, which depends upon the column, x, and the molecular structure of the various compounds, y. The values of $K_{x,y}$ for the A, C, and D stages are shown in the tabulation below.

Stage	$K_{x,y}$	(inches²/mole %)
C	0 85[a]	
A	Aliphatics = 31	Cyclics = 27
D	Aliphatics = 50	Cyclics = 45

[a] Except for hydrogen.

The B-stage low-concentration, constant-linear-slope values for $K_{x,y}$ are plotted against carbon atoms per molecule in Fig. 7. At higher concentrations of the early (through C_4) peaks, Eqs. (2) and (3) are not applicable because HW_1/mole % falls off.

Oversize sampling for trace analysis also broadens peaks to the extent that additional time is needed to sweep the sample plug into the A column; e.g., the half-widths of median B column peaks more than double when sample pressure is raised to 30 psig.

Hydrogen is unique in that it undergoes peak reversal (*8*, *22*, *23*). But up to this point (*24*) calibration data can be plotted, as shown in Figure 8. Above 35 mole per cent, hydrogen usually is determined either by difference, or by mass spectrometry, although a smaller sample could be used.

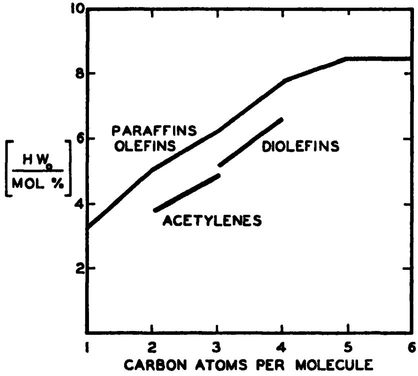

FIG 7. B-stage quantitative relations (3.6 cc sample).

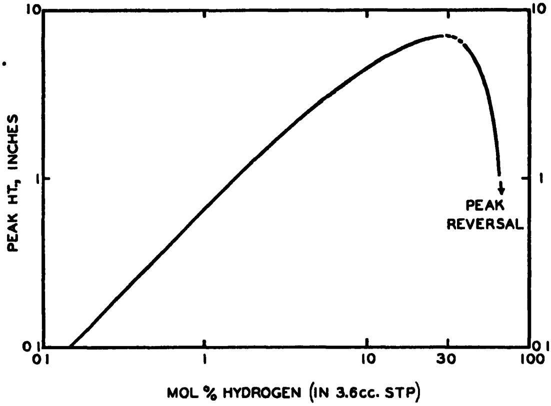

FIG. 8. C-stage hydrogen calibration.

The following relation (*25*) also is useful over moderate retention ranges:

$$\frac{W_0}{T_0} = K'_{x,y} \tag{4}$$

where T_0 = normal (low concentration) distance from sample entry to peak maximum, inches; and $K'_{x,y}$ = a dimensionless constant, and subscripts x and y have the above connotation.

These relationships were used to spot data irregularities, to smooth scattered data, and to make occasional interpolations.

TABLE IX
D RETENTIONS FOR A-TO-D ROUTING OF C_1–C_5's

Compound	Emergence time, minutes	Relative retention
Air	1.70	0.121
Ethane	2.06	0.146
Ethylene	2.09	0.148
Carbon dioxide	2.31	0.164
Propane	2.96	0.210
Propylene	3.32	0.236
Acetylene	3.96	0.281
Isobutane	4.35	0.309
Propadiene	5.75	0.41
n-Butane	5.75	0.41
1-Butene	6.61	0.47
Isobutene	6.61	0.47
trans-2-Butene	7.90	0.56
cis-2-Butene	8.90	0.63
Propyne	9.05	0.64
1,3-Butadiene	10.7	0.76
3-Methyl-1-butene	10.9	0.77
Isopentane	10 9	0.77
n-Pentane[a]	14.1	1.00

[a] 2800 theoretical GC plates.

The C peaks are unique in the absence of the rare gases neon, argon, and krypton. The identities of the B peaks usually are unequivocal because NH_3, H_2S, and SO_2 are absorbed by the column, and acetylene, neopentane (2,2–dimethylpropane), propadiene, and propyne are unlikely in refinery gases and normally are presumed absent. When these are suspected, all but the neopentane can be rearranged by routing the early peaks from the A to the D column, rather than to B as normally scheduled; pertinent A-to-D retentions are shown in Table IX.

The peaks that appear on both the A and D charts must be matched for both retentions and percentages. The A recorder's pipping-pen integrator permits quantitative estimation of the total represented by overlapping A peaks, and is useful for the broadened C peaks. Readout is as shown in the following tabulation.

Detector	Molecular type	Pips/Mole %
A	Aliphatic hydrocarbons	23,000
	Cyclic hydrocarbons	21,000
C	Inorganic gases	720

Unresolved conflicts are listed in Table X. H_2O is seldom discerned and does not interfere because its sensitivity is very low and because the front side of its peak has a very low constant slope; it returns to baseline sharply at a distance that is a function of its concentration. The sum of the individual components should total 100%. Actual totals (see Table XII) generally range from 98 to 102%, and occasionally from 95 to 105%. These totals shift gradually. When a negative gap occurs it can be assigned to slowly eluted compounds like benzene that are not sought normally, or to $>35\%$ of hydrogen if its peak has reversed. These can then be estimated by difference, using the totals from adjacent runs. A deficiency may also result from the unusual and unrecognized presence of low-sensitivity acetylene or propyne. The apparent percentages are normalized, usually on an air-free basis. Depending on the complexity of the analyses, chart reading and calculations may require from several minutes to several hours.

TABLE X

UNRESOLVED CONFLICTS ON THE FOUR-STAGE GAS CHROMATOGRAPH[a]

Hydrocarbon type	Conflicts	Carbon atoms per molecule	Identity
Paraffins	1	4 and 5	*n*-Butane and 2,2-dimethylpropane
	1	6	2,3-Dimethylbutane and 2-methylpentane
Cycloparaffins	0	—	—
Cycloolefins	0	—	—
Monoolefins	5	6	3- and 4-Methyl-1-pentene
			trans- and *cis*-4-Methyl-2-pentene
			trans- and *cis*-3-Hexene[b]
			1-Hexene and 2-methyl-1-pentene[b]
			trans-2-Hexene and 2-ethyl-1-butene[b]
Diolefins	2	3 and 4[c]	Propadiene and isobtuene
		5	1,2- and 2,3-Pentadiene
Acetylenes	2[c]	2 and 4	Acetylene and *n*-butane
		3 and 4	Propyne and 1,3-butadiene

[a] Listed as though subsequent classes were absent to avoid duplication.

[b] One can be identified if the other is absent.

[c] Resolvable by A → D routing.

Typical Analyses

Analyses of samples containing large amounts of a few components are shown in Table XI, using Phillips Hydrocarbon Mixtures Nos. 31 and 38. Analysis of a wide-range Phillips Mixture, No. 41, appears in Table XII. Trace amounts of many compounds not reported by Phillips are detected. The other analyses in Table XIII were selected to show a wide range of

TABLE XI

ANALYSES OF PHILLIPS HYDROCARBON MIXTURES NOS. 31 AND 38

Compounds	Mixture No. 31		Mixture No. 38	
	Phillips[a]	4-GC[b]	Phillips[a]	4-GC[b]
		(mole %)		
Carbon dioxide				0.002
Ethane		0.003		
Propane	38.51	37.9	12.09	11.3
Isobutane	14.66	14.8	15.50	15.8
n-Butane	44.63	45.0	31.35	31.6
2,2-Dimethylpropane			0.08	
1-Butene				0.03
Isobutene				0.03
trans-2-Butene				0.03
Isopentane	2.20	2.2	13.56	13.8
n-Pentane			27.32	27.3
Cyclopentane			0.10	0.03
1-Pentene				0.02
trans 2-Pentene				0.02
2-Methyl-1-butene				0.02
2-Methyl-2-butene				0.02
2,2-Dimethylbutane				0.01
2,3-Dimethylbutane 2-Methylpentane				0.02
n-Hexane				0.005
2,2-Dimethylpentane				0.02
	100.00	99.9	100.00	100.06

[a] ±0.05% wt

[b] 3.6-cc STP sample

TABLE XII

ANALYSES OF PHILLIPS HYDROCARBON MIXTURE NO. 41

Compounds	Analyses, mole %				
	Four-stage gas chromatograph[a]				Phillips[b]
	1	2	3	Avg	
Carbon dioxide	NS	0.006	0.005	0.006	—
Propane	6.4	6.4	6.3	6.4	6.27
Isobutane	10.5	10.3	10.2	10.3	10.76
n-Butane	25.7	25.3	25.2	25.4	25.10
1-Butene	10.9	11.0	10.8	10.9	11.61
trans-2-Butene	5.8	5.8	5.7	5.8	5.99
cis-2-Butene	0.01	0.01	0.01	0.01	—
Butadiene-1,3	NS	0.01	0.01	0.01	—
n-Pentane	4.9	5.0	4.9	4.9	4.75
1-Pentene	1.99	1.97	2.01	1.99	1.98
2-Methyl-1-butene	0.02	0.02	0.02	0.02	0.02
trans-2-Pentene	0.005	0.002	0.003	0.003	—
2-Methyl-2-butene	0.003	0.003	0.003	0.003	—
2-Methylpentane	9.7	10.5	10.5	10.2	9.92
3-Methylpentane	0.08	0.09	0.09	0.09	0.10
n-Hexane	8.7	9.2	9.1	9.0	8.68
Methylcyclopentane	0.03	0.09	0.09	0.07	—
Cyclohexane	7.4	6.8	7.0	7.1	7.02
3-Methylhexane	0.03	0.04	0.03	0.03	—
2,4-Dimethylpentane	0.02	0.01	0.01	0.01	0.03
3,3-Dimethylpentane	0.01	0.02	0.01	0.01	—
n-Heptane	7.7	7.4	7.8	7.6	7.75
cis-1,2-Dimethylcyclopentane	NS	NS	NS	NS	0.02
	99.91	99.97	99.79	99.85	100.00
Actual total, before normalizing, including air	101.6	99.5	100.2	100.4	—

[a] 3.6-cc STP sample; NS means "not sought."

[b] ±0.05% wt.

TABLE XIII

OTHER FOUR-STAGE GAS CHROMATOGRAPHY ANALYSES, MOLE %

No.	Compound	Re-former off-gas	Off-gases from H_2-treated resids		B-B feed	Pyrolysis vapor	Pyrolyses C_5 cuts (IBP to 110°F)		No.
							(Low temp. Pod)	(High temp. Pod.)	
1	Hydrogen	98.0[a]	98.0[a]	64.2[a]		12.0			1
2	Oxygen	0.04	0.13	0.02					2
3	Nitrogen	0.32	0.96	1.20					3
4	Carbon monoxide		0.01	0.31					4
5	Carbon dioxide	0.04	0.07	0.47				0 01	5
6	Carbonyl sulfide					0.003			6
7	Methane	0.02	0.34	14.5		21	0.08		7
8	Ethane	0.02	0.12	6.8	0.002	7.2	0.48	0.03	8
9	Ethylene		0.02			24	1.37	0.02	9
10	Acetylene[b]	NS	NS	NS		0.12		NS	10
11	Propane	0.19	0.09	5.7	7.3	0.51	0.28	0.32	11
12	Cyclopropane					0.007			12
13	Propylene		0.03	0.49	2 1	15.8	8.8	0.59	13
14	Propadiene[b]	NS	NS	NS		0.10	0.16	NS	14
15	Propyne[b]	NS	NS	NS	0.09	0.08	0.85	NS	15
16	Isobutane	0.28	0.01	0.98	27	0.03	0.06	0.01	16
17	*n*-Butane	0.22	0.05	1.94	25	0.05	0.12	0.10	17
18	1-Butene		0.01	0.13	6.8	2.1	5.1	0.87	18
19	Isobutene		0.01	0.15	10.3	2.0	5.3	13.4	19
20	*trans*-2-Butene		0.01	0.17	8.6	0.57	1.94	0.26	20
21	*cis*-2-Butene		0.01	0.11	7.0	0.47	1.94	0.18	21
22	1,3-Butadiene					1.86	5.9	3.9	22
23	1,2-Butadiene						0.32	0.37	23
24	Isopentane	0.36	0.02	0.67	3.8	0.52	3.3	0.02	24
25	*n*-Pentane	0.14	0.03	0.78	0.74	4.6	38	4.5	25
26	Cyclopentane	0.02	0.01	0.05		0.65		0.10	26
27	1-Pentene		0.001	0.06	0.47	0.29	2.7	0.27	27
28	*trans*-2-Pentene		0.003	0.10	0.17	0.17	1.8	3.4	28
29	*cis*-2-Pentene		0.002	0.05	0.09	0.08	0.97	1.44	29
30	2-Methyl-1-butene		0.002	0.05	0.58	0.28	3.8	3.1	30
31	2-Methyl-2-butene		0.004	0.11	0.27	0.11	0.97	5.4	31
32	3-Methyl-1-butene							0.5	32
33	Cyclopentene				0.02	0.06		0.28	33
34	2-Methyl-1,3-butadiene						4.4	54	34

TABLE XIII. Continued

No.	Compound	Re-former off-gas	Off-gsaes from H_2-treated resids		B-B feed	Pyrol-ysis vapor	Pyrolyses C_6 cuts (IBP to 110°F)		No.
							(Low temp. Pod)	(High temp Pod)	
35	2,3-Pentadiene							2.2	35
36	1-*cis*-3-Pentadiene							1.3	36
37	1,3-Cyclopentadiene						6.8		37
38	2,2-Dimethylbutane	0.22				0.14			38
39	2,3-Dimethylbutane	0.08	0.01	0.25		1.23			39
40	2-Methylpentane								40
41	3-Methylpentane	0.04	0.01	0.11		0.69			41
42	*n*-Hexane	0.02	0.01	0.23	0.005	1.1	0.89		42
43	Methylcyclopentane		0.01	0.07		0.42			43
44	Cyclohexane			0.01		0.69		0.03	44
45	1-Hexene			0.03		0.07	0.17	0.27	45
46	2-Methyl-1-pentene								46
47	*trans*-2-Hexene			0.04					47
48	*trans*-3-Hexene			0.04			3.0	2.6	48
49	2-Ethyl-1-butene								49
50	3-Methyl-1-pentene				0.01				50
51	4-Methyl-1-pentene								51
52	2,3-Dimethyl-2-butene							0.09	52
53	1,5-Hexadiene						0.2	0.14	53
54	Benzene					0.4			54
55	2-Methylhexane			0.05		0.07			55
56	3-Methylhexane			0.05		0.03		0.02	56
57	2,4-Dimethylpentane					0.45			57
58	3,3-Dimethylpentane							0.02	58
59	2,2,3-Trimethylbutane							0.03	59
60	*n*-Heptane			0.06				0.07	60
61	1-Methylcyclopentene							0.09	61

[a] Hydrogen determined by difference; four times usual sample taken (14 cc STP).

[b] By supplementary gas chromatography; NS indicates "not sought"

concentrations and unusual components; only one of these is amenable to analysis by mass spectrometry directly.

Trace analysis of high-purity propylene is illustrated in Table XIV.

Repeatability and Accuracy

Precision of the four-stage gas chromatograph varies with the peak height per mole per cent of the various compounds. For example, the D-

TABLE XIV

TRACE ANALYSIS OF PURE PROPYLENE

Compound	Mole %
Methane	0.001
Ethane	0.35
Acetylene[a]	0.001
Propane	0.02
Propadiene[a]	0.0003
Methyl acetylene[a]	0.001
Propylene, by difference	99.63
	100.00

Note: Sample quantity: 27 cc at 30 psig (72 cc STP).

[a] Absence of conflicting compounds determined by A → D flow routing

stage peak height per mole per cent for *trans*-2-pentene is 52 inches, vs 7 inches for *n*-heptane, so that for similar amounts the pentene can be determined about six times as precisely as the *n*-heptane. This is reflected by the number of significant figures posted for these data in Table VII. Thus, precision is estimated to range from ±2% to ±5% of the amounts present down to peak heights of about 1 inch, and from ±0.03 to ±0.1 inches for the early and late peaks, respectively. Accuracy is estimated to be twice the precision.

The precision of results (other than by difference) are generally indicated by reporting them as in the data given below.

Per cent of sample	Number of Digits
0.000 to 0.09	One
0.10 to 0 99	Two
1 00 to 1 99	Three
2 0 to 99	Two

The replicate analyses of Phillips No. 41 in Table XII illustrate the system's repeatability, and Tables XI and XII indicate its accuracy.

DISCUSSION

The working life of the columns and thermistors are estimated to be of the order of 1 to 2 years. The present system has been in routine service for a year and a half, during which a few components have been replaced. Column aging has been accompanied by slowly decreasing retention (ca. 5%/yr). On the other hand, a somewhat greater increase in detector sensitivity parallels thermistor aging. However, these changes are gradual so that satisfactory corrections can be made by suitable proportioning. (Occasional calibration checks are advisable).

An unidentified peak usually appears ahead of the regular peaks on the C system. This can be seen in Figure 4. It is not associated with the presence of hydrogen, and its cause presently is not known.

Retentions measured from sample entry are obviously most useful for this system. Air times are given, however, so that dead time corrections can be made for comparative purposes. The number of digits used to express retentions are chosen primarily to indicate the relative positions of neighboring peaks; their significance falls off as the spread between peaks increases.

The correctness of retention data for the later peaks can be conveniently verified by plotting the logs of their air-corrected retentions ("delays") in

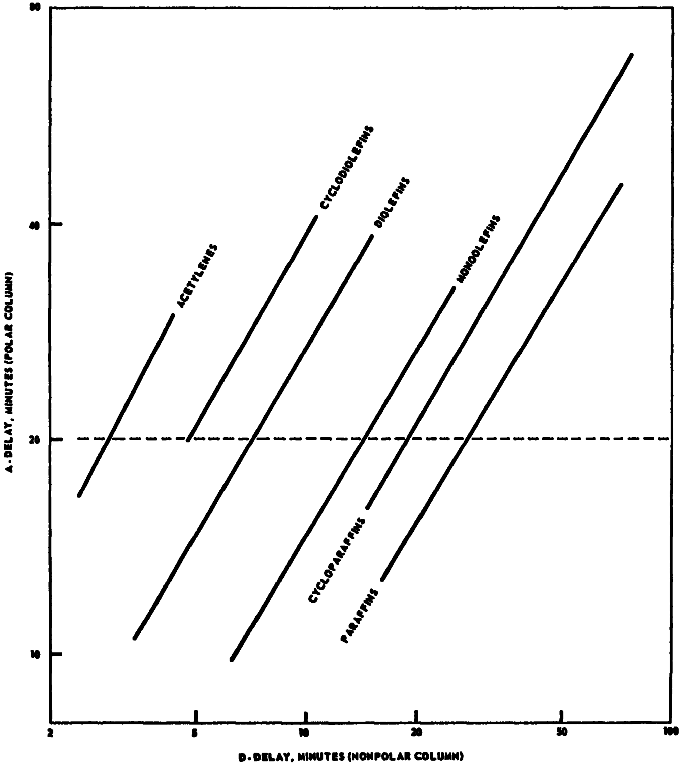

FIG. 9. Hydrocarbon types from polar and nonpolar retentions.

the polar A column against those for the nonpolar D column, after Pierotti *et al.* (*26*). The resulting straight, parallel lines are shown in Fig. 9 and may be characterized by the D-delays[1] corresponding to a median A-delay value of 20 minutes:

Hydrocarbon type	D-delay (minutes) for A-delay = 20 minutes
Acetylenes	3
Cyclodiolefins	5
Diolefins	7
Cyclomonoolefins	10
Monoolefins	14
Cycloparaffins	18
Paraffins	27

Unknown hydrocarbons can be typed in this way, and their boiling points estimated from retention data. The number of carbon atoms per molecule can also be estimated for each type by plotting carbons per molecule against the log of retention (*27*).

Our relative sensitivities generally are consistent with those of Rosie and Grob (*28*), and Messner, Rosie and Aragabright (*29*). However, we obtain better agreement with their data C_1–C_5 by using HW_1 in place of planimetered area (*30*); and we find HW_1/mole % to be more constant than Area/mole % over a range of C_5–C_7 compounds.

The previously mentioned relation between theoretical GC plates and resolution is based on the peak geometry obtained with our direct flow detectors. The projected base (length of base line cut out by two tangents to the points of inflection) of these peaks is consistently equal to about 1.66 times their normal half-widths:

$$\text{Projected base} = 1.66\ (\text{half-width}) \tag{5}$$

$$\text{Peak sharpness} = \text{retention/half-width} \tag{6}$$

$$\text{Theoretical GC plates} = 16\ (\text{retention/projected base})^2 \tag{7}$$

Combining Eqs. (5), (6), and (7):

$$\text{Theoretical GC plates} = 5.8\ (\text{peak sharpness})^2 \tag{8}$$

Littlewood (*31*) reports a similar expression, except that his constant, 5.54, was derived from the Gaussian error function. He reports values up to 10% lower than Eq. (8), whereas Eqs. (7) and (8) agree within measurement errors.

Equation (5) can also be used as a basis for estimating the normal position of peaks whose maxima are displaced by the skewness associated with

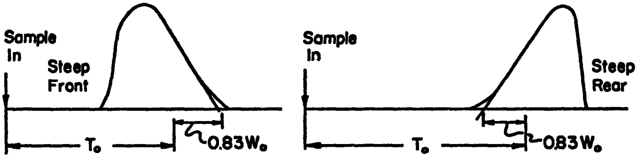

FIG. 10. Estimation of normal retention of peaks displaced by overloading.

overloading. It is reasonable to assume that the less steep side of an overloaded peak is its normal slope. The correct location of such a peak can then be found by cutting the base line with a tangent to the less steep side of the peak and laying off $\left(\frac{1.66\ W_0}{2}\right)^2 = 0.83\ W_0$ toward the peak maximum (see Fig. 10).

Overloaded peaks may have a slight "echo" in the next run; more than about 2½ cc STP of any one compound (70% of a normal sample) will show a small peak (~0.03%) in the next run. This probably could be eliminated by avoiding plastic elements in the sample entry toggle valves.

The greatest limitation of this system lies in the length of time required to determine benzene, and the consequent low sensitivity. Introduction of a fifth detection point after the first foot of PS:DMS (A) column would correct this; and provision could also be made at this point for backflushing heavy constituents from the system (*32*). This implies, of course, direct injection of liquid-phase samples.

Better control of temperature, bridge voltage, and column exit pressure (atmospheric pressure varies over a range of 3%) will improve precision and accuracy. Also, the use of hydrogen instead of helium is expected to halve pressure drop, operating time, and carrier gas consumption (*33*) at the expense of direct determination of hydrogen in samples.

SUMMARY

Mixtures of complementary partitioning liquids and a four-stage gas chromatographic system make possible routine analyses for H_2, O_2, N_2, CO, COS, CO_2 and more than 70 hydrocarbons with few conflicts. Lower detection limits range from 0.0001 to 0.02%, with definite identifications. C_6's and C_7's can be summated by a recording integrator. NH_3, H_2O, H_2S, and SO_2 are not included but do not interfere.

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CHAPTER XVI

A High-Temperature Gas Chromatograph

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INTRODUCTION

A laboratory gas chromatograph operating in the range of 50° to 500°C has been developed. The instrument is of modular design and consists of an analyzer and a separate control unit. This method of construction permits one or more analyzers to be used with and regulated by a single control unit. The control unit contains the power input and distribution system, the carrier gas flow-controlling and metering system, and the detector circuit controls.

DESCRIPTION

The analyzer module only will be discussed here. The analyzer consists of an insulated oven section and a ventilated space for the thermostat and electrical controls, as shown in Figs. 1 and 2. A perforated cover allows air to circulate under and around the oven section. In this way the outer case and electrical components stay reasonably cool.

PROBLEMS

The main problems encountered in the design of this type of instrument were: (a) The choice of suitable corrosion-resistant materials for components such as the heat sink and fittings; (b) developing a high-temperature detector seal; (c) regulation of oven temperature; (d) providing efficient thermal insulation and heat-resistant electrical insulation; (e) sample introduction system.

The methods and materials employed in the construction of the analyzer are outlined in the following sections.

Material Selection

The materials subjected to a temperature of 500°C must be carefully chosen to perform their function in the instrument and, at the same time, be resistant to corrosion for a number of years of use.

The column, detector block, and sample injection blocks are made of stainless steel which will easily withstand this temperature. Stainless steel tubing is used throughout and is welded at the points where it joins with

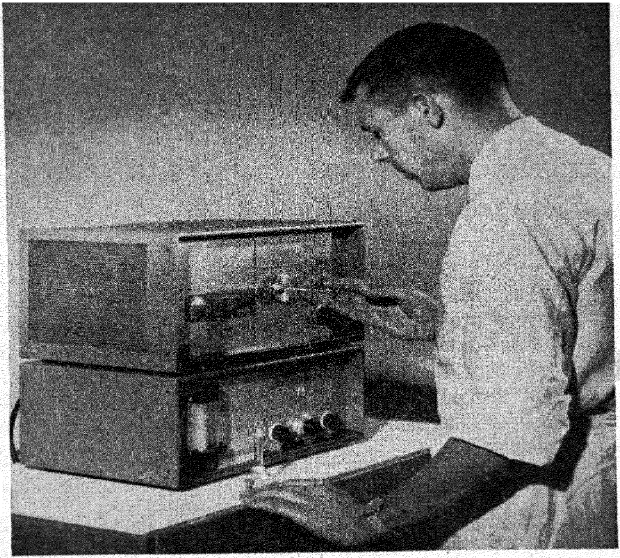

FIG. 1. Analyzer of high-temperature gas chromatograph.

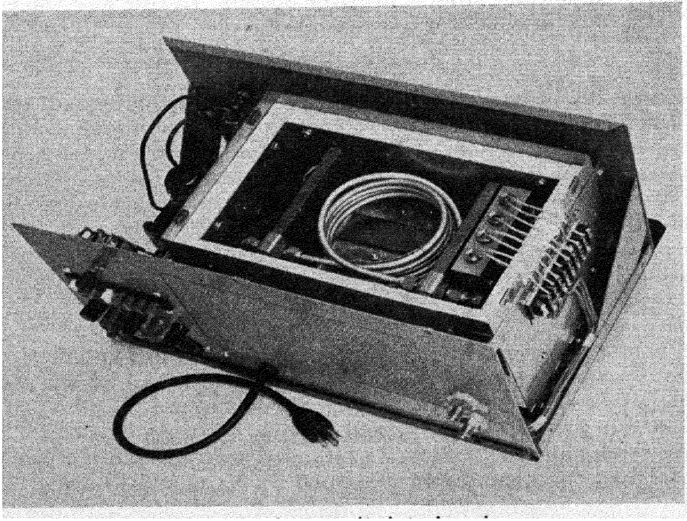

FIG. 2. Analyzer unit, interior view.

the detector block. Copper-gold brazing is used to join the capillary tube to the injection block. The above components are mounted on a heat sink which serves to stabilize the oven temperature with its large heat capacity.

Aluminum is an ideal heat sink material below 400°C, but reaches its softening point under 500°C. A high-grade bronze casting was tried for the prototype model heat sink, but was found to be unsuitable due to heavy oxidation and scaling. The material chosen was aluminum bronze, (composition: aluminum 87%, copper 10%, iron 3%). This material has excellent heat capacity and conductivity, is easily machinable, and shows only slight discoloration after extended use at 500°C.

All fittings are of the stainless steel Swagelock type. In places where the fitting may require frequent disconnection, nuts and ferrules of Monel are used. Stainless to stainless threads tend to jam at high temperatures even when lubricated.

Detector Seal

The detectors consist of four heated thermal conductivity elements arranged in a bridge configuration. Each element consists of a spirally wound filament of nickel-iron wire. The filament is supported by a feed-through insulator assembly consisting of two wires and a flanged header sealed by a specially developed high-temperature glass. Monel nuts are used to clamp the detector headers into the stainless steel detector block.

Temperature Regulation

The oven temperature is regulated to within ±0.5°C and is continuously adjustable through the range of 50° to 500°C.

Cartridge heaters are housed in the lower part of the heat sink and provide steady and cycling heating. The steady heaters are controlled by push buttons which select one of four heat ranges. The cycling heater is regulated by a sensitive thermostat control.

Thermal and Electrical Insulation

The oven is insulated by silicone-impregnated Fiberglas of 6-lb/cu ft density, ¾ inch thick, sandwiched between stainless steel sheets. The edges of the Fiberglas are fitted tightly to prevent air leakage causing uneven heat distribution.

All the components in the oven are mounted on the heat sink. The assembly is supported by stainless steel standoffs resting on Supramica blocks which reduce heat conduction to the outer case. The oven top is easily removed for column changing and replacement of detectors. For access to the other components, the oven walls can be detached.

The detector leads are electrically insulated between the headers and the terminal block by a double layer of high temperature Fiberglas sleeving.

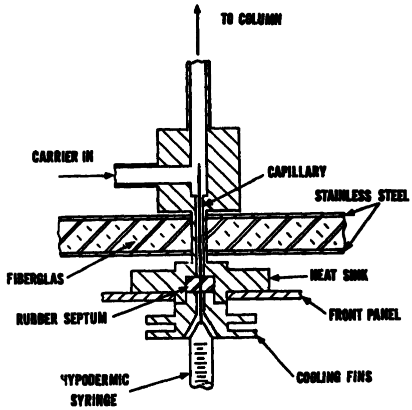

FIG 3. Sample injection system.

The heater leads are insulated by silicone rubber-impregnated Fiberglas. At high temperatures this material soon dries out and cracks. Therefore, within the oven the leads are reinforced with an extra sleeving of woven ceramic fiber.

Sample Introduction

Samples are injected into the system by a precision hypodermic syringe, usually of 5- or 10-μl capacity. The 3-inch hypodermic needle passes through a self-sealing silicone rubber septum connected to the injection block by a stainless steel capillary tube. Samples are deposited directly into the heated carrier stream ahead of the column (see Fig. 3).

The small amount of heat transmitted through the capillary is rapidly dissipated into the front panel and radiated by cooling fins on the inlet nozzle. The septum is kept relatively cool and does not require frequent replacement.

Columns

Columns are easily interchangeable, and up to 50 ft of ¼ inch tubing can be accommodated. Stainless steel tubing is recommended for high-temperature work, as copper scales badly above 300°C.

Column Packings

A limited number of columns have been tested with sufficiently low vapor pressures and stability for use at high temperatures. Some of these, and their approximate maximum operating temperatures, are:

Apiezon L grease	350°C
Silicone high vacuum grease	350°C
Asphaltenes	400°C
Silicone rubber	500°C
Fused salts	500°C
Metal stearates	—
Polyethylene	—
Adsorbents	
Alumina, silica gel, charcoal, florasil, zeolites	500°C

Applications

A limited amount of application work has been performed to date at column temperatures up to 500°C. It is to be expected that thermal cracking will occur in the columns, since some of the temperatures involved are well

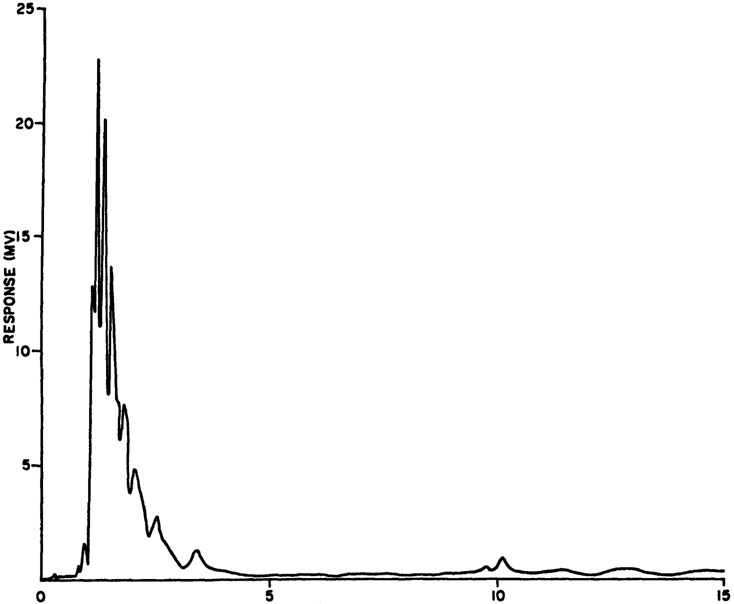

Fig. 4. Chromatogram of crude oleyl alcohol. Column temperature: 350°C.

above the cracking points of the more heat-sensitive compounds. Th cracking has been evidenced by the appearance of peaks apparently n those of the parent compound, and by laying down of carbon on the colun packing. It has not yet been determined whether the cracking patterns a repeatable.

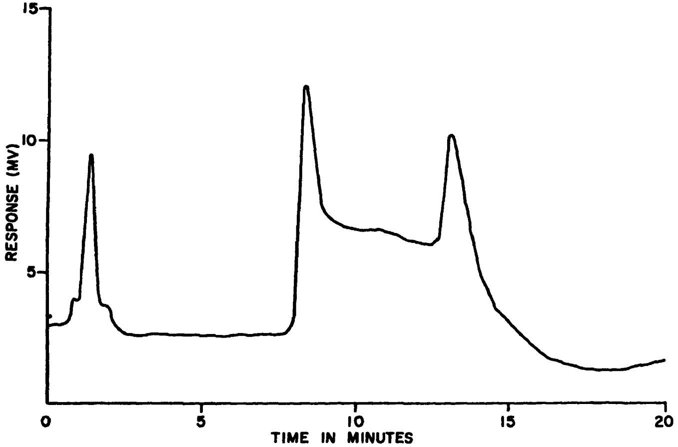

Fig. 5. Chromatogram of isopropyl diphenyl. Column temperature: 460°C.

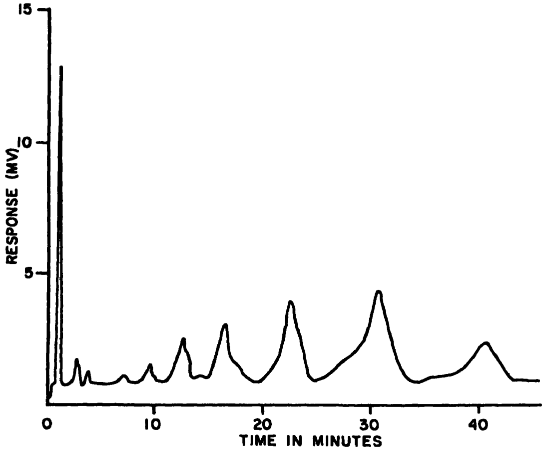

Fig. 6. Chromatogram of sperm oil. Column temperature: 360°C.

Another effect noted has been a disturbance of the base line following appearance of the first peaks, with a gradual recovery over a 10- to 30-minute period. The displacement may be negative or positive. It occurs with the more heat-sensitive materials at column temperatures above 350°C. With the more stable materials, such as polyaromatic heat-transfer agents and high-temperature lubricants, it does not occur even at 500°C. The effect is assumed to be caused by cracking and deposition of cracked products at the filaments, which may operate at temperatures several hundred degrees higher than the column.

Figure 4 is a chromatogram of a crude oleyl alcohol sample, run at 350°C. Figure 5 is a sample of isopropyl diphenyl, run at 460°C. Solids such as this are dissolved in a suitable solvent so as to make it possible to inject them by hypodermic syringe. The first peak shown is that of the solvent. The previously mentioned effect of base line disturbance can be seen following the second main peak. Figure 6 is a sample of sperm oil run at 360°C.

SUMMARY

We have presented a description of the problems encountered in the design of a chromatograph analyzer for high-temperature use. The analyses of components with boiling points up to 600°C were also discussed.

CHAPTER XVII

Separation and Identification of Oxygenated Hydrocarbons in Combustion Products from Automotive Engines

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INTRODUCTION

Published reports (*1–4*) have shown that gas chromatography has been successfully applied to the analyses of a number of classes of oxygenated compounds. Also, chromatographic methods have been described for analyzing partly oxidized hydrocarbons (subsequently referred to as "oxygenates") in preflame mixtures (*5*, *6*). However, very little information has been published on the application of these methods to the analysis of oxygenates found in the combustion products from an automotive engine. This report will discuss preliminary studies using gas chromatographic equipment for separating and identifying oxygenates that are found in such combustion gases.

These products of combustion are a complex mixture of water, fixed gases, hydrocarbons, and oxygenates, in which the latter usually occur in relatively low concentrations. In the elution of components of such a mixture from a gas-liquid partition chromatographic (GLPC) column which separates components on a boiling-point basis, the small amounts of oxygenates will be obscured by water and hydrocarbons. Thus, to determine the oxygenates it was necessary to make a gross separation of them from other materials. Chemical drying agents were unsuitable because they reacted with a significant quantity of the oxygenates and, therefore, the necessary class separations were sought using chromatographic techniques.

The problem was resolved satisfactorily by using a three-stage chromatographic unit to make gross separations of hydrocarbons, oxygenates, and water. However, greater resolution of some oxygenated fractions was required, and this was accomplished by recovering fractions from the three-stage unit and introducing them into an additional single-stage analyzer.

EXPERIMENTAL PROCEDURES AND RESULTS

GLPC Analytical Equipment

The staged chromatographic equipment discussed in this paper was specifically developed for analyzing wide boiling-range mixtures. With such a system it is possible to achieve as much individual component resolution

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as is necessary and at the same time to monitor all sample components. In addition, after a given analysis is completed, the system is immediately ready for the introduction of another sample.

The three-stage apparatus used in these studies includes a glycerol column in the first stage to retain oxygenates for a longer time than hydrocarbons of corresponding boiling point. This column effectively holds water so that it does not enter the second and third stage. The second stage, also a polar column, helps to make an over-all separation of hydrocarbons and oxygenates. This second-stage column elutes all hydrocarbons through *n*-heptane ahead of low-boiling oxygenates. The third stage, a nonpolar silicone column treated with stearic acid to reduce tailing, is suitable for general separation of components in the mixture, as well as for analyses of fatty acids.

Under the operating conditions stated herein, the general range of oxygenates that can be handled by the three-stage GLPC system covers ethylene oxide through *n*-pentanol. The resolution of the single-stage analyzer is superior to that obtained with the multiple-staged unit, but its analytical range is generally limited to materials retained no longer than *n*-propanol.

Three-Stage Chromatograph

Figure 1 is a flow diagram of the three-stage GLPC system employed in these studies. By manipulating a four-way valve, each stage can be operated independently of the previous stage. This makes it possible to exclude from the second and third stages those materials that cannot be eluted in an acceptable time, which has been found to be about 2 hours. After a sample stream is diverted from a stage, carrier gas is introduced from a separate source to continue elution of materials already in the stage. Flow restrictions in the inlet and outlet of the separate stages may be adjusted so that the stages can be shifted in or out of series with virtually no disturbance registered by any of the three detectors.

The temperature of detectors and columns is maintained with a constant temperature air bath. Power input to the bath heaters is regulated by an adjustable transformer which allows for coarse control of the bath temperature. Fine control is accomplished with a bimetallic switch; this switch alters the grid bias on a 3C23 gas tube which acts as a relay to provide electrical power to a string of 6-volt automobile headlight bulbs (GE 87). The bulbs were chosen for their low thermal inertia, and because their heavy filaments are capable of withstanding the rapid on-off heating cycles. This system is capable of controlling the bath temperature within ±0.05°F. Detector elements are 8000-ohm thermistor beads mounted in a brass block 2 × 2 × 2 inches. The beads are located just above the direct helium stream.

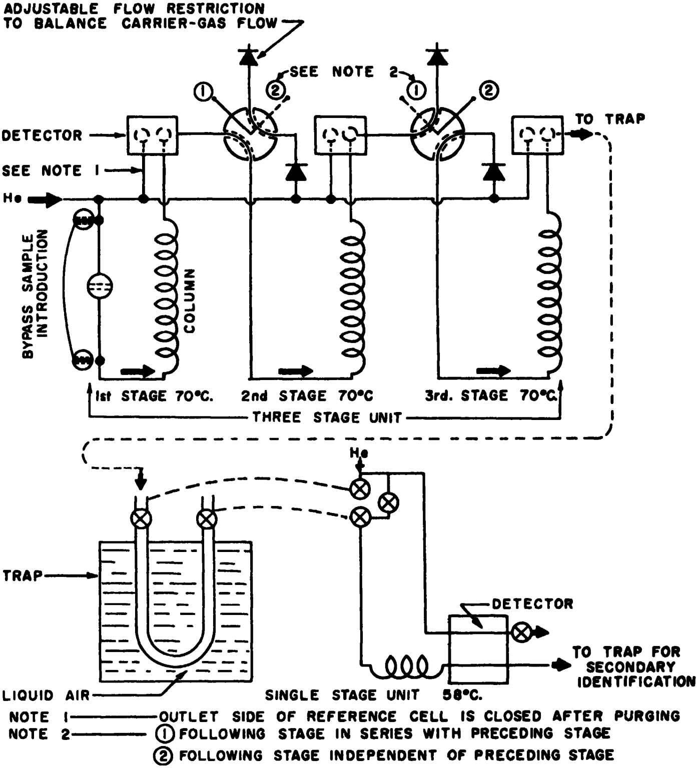

FIG. 1. Flow schematic of GLPC analytical system.

Teflon plugs are used in the four-way valves and need no lubrication. The adjustable restrictions are throttling-type needle valves.

The columns and operating conditions are as follows:

Helium carrier gas flow, 80 ml/min through each stage, as measured at atmospheric pressure.

First Stage:	Temperature, 70°C; pressure at head of stage, 10.7 psig.
4 ft	20–28 mesh J-M C-22 firebrick treated with glycerol in the weight ratio 20 parts liquid to 100 parts solid. Total weight packing, 12 gm.
Plus 6 ft	30–50 mesh firebrick treated with polyethylene glycol 400, 20/100. Total weight packing, 15 gm.

Second Stage: Temperature, 70°C; pressure at head of stage, 4.5 psig.
5 ft 40–50 mesh firebrick treated with PEG 400, 20/100. Total weight packing, 12.5 gm.

Third Stage: Temperature, 70°C; pressure at head of stage, 2.7 psig.
5 ft 20–28 mesh firebrick treated with D.C. 550 silicone oil, 20/100 plus 2 parts stearic acid to 100 parts dry solid. Total weight packing, 15 gm.

All columns are made of standard ¼ in. OD stainless steel tubing.

Single-Stage Chromatograph

This unit, built in the Bureau of Mines laboratories, uses a constant temperature air bath. Coarse control of the bath temperature is provided with an adjustable transformer which controls electrical input to the main bath heater. Fine temperature control is accomplished using a thermistor-actuated saturable reactor to control a low wattage electrical heater. A thermistor is used in the system as the temperature-sensing element. These controls are capable of maintaining bath temperature to ±0.15°F. To prevent this temperature fluctuation from affecting the detector output, the cell is immersed in buckshot. This increases the mass of the cell assembly and serves to decrease the temperature fluctuation of the thermistor elements. Detector block and thermistor elements are the same as described for the three-stage chromatograph. The sample introduction valves are a toggle action diaphragm type; the entire system, excluding the detector block, is made of stainless steel to reduce interactions with the oxygenates.

The columns and operating conditions are as follows:

Helium flow measured at outlet, 80 ml/min; temperature, 58°C.

20 ft 40–50 mesh J-M C-22 firebrick treated with Reoplex 400 (Geigy Pharmaceuticals, Ardsley, New York) in the weight ratio 30/100. Weight packing, 66 gm. The column is made of ¼ in. OD stainless steel tubing.

EXPERIMENTAL RESULTS

Figure 2 is a chromatogram obtained using a mixture of known composition; it illustrates separation characteristics of the three-stage chromatograph with the analysis of a test mixture. The components of the blend are typical of those found in combustion products, except that the hydrocarbons normally are present in much higher concentration than the oxygenates. It will be observed from the second-stage chromatogram that hydrocarbons with boiling points below that of isooctane emerge before low-boiling oxygenates such as ethylene oxide. With staged GLPC equipment it is possible to divert this fraction from following stages and thereby

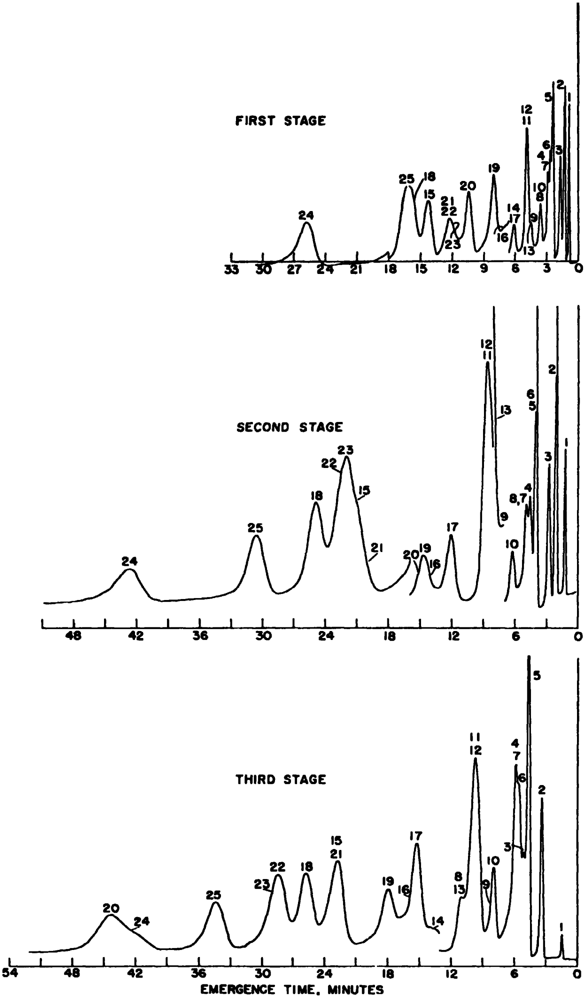

FIG. 2. Separation characteristics of three-stage chromatographic unit. 1: air; 2: *n*-hexane; 3: isooctane; 4: acetaldehyde; 5: ethylene oxide; 6: methylal; 7: propylene oxide; 8: *n*-octane; 9: propionaldehyde; 10: 1,1-dimeoxyethane; 11: acetone; 12: acrolein; 13: diethoxymethane; 14: butyraldehyde; 15: methanol; 16: crotonaldehyde; 17: benzene; 18: ethanol; 19: 3-me-2-butanone; 20: *n*-decane; 21: 2,3-butanedione; 22: meisobutyl ketone; 23: toluene; 24: propanol; 25: isovaleraldehyde. Helium flow: 80 ml/min; temperature: 70°C.

remove hydrocarbons which may interfere with oxygenates in later stages. *n*-Octane and *n*-nonane may interfere with detection of some lower boiling oxygenates, such as propylene oxide and propionaldehyde. However, a more serious problem will be found with branched C_{10} and C_{11} paraffins tending to cover oxygenates ranging from *n*-butyraldehyde through *n*-propanol. This range includes the major portion of oxygenates that have been identified thus far in these studies.

The principal advantage of a three-stage analyzer, as shown in Fig. 2, is that it allows a broad scanning of those compounds existing in the original sample. In addition, it allows identification of unknown peaks, with three different retention-time measurements. This can be a substantial aid in the analysis of a complex mixture. Nevertheless, resolution of individual compounds as accomplished by the staged unit is still not sufficient for good quantitative analytical determinations. Therefore, fractions are recovered from the three-stage chromatograph for reanalysis with a single-stage unit; separation characteristics are shown in Fig. 3.

Ethylene oxide and acetaldehyde, as shown in Fig. 3, are not separated, but this depends largely on their relative magnitudes. Methylal and propylene oxide are not resolved, but usually methylal is no more than a minor component of combustion products. There are other instances in which important compounds are not resolved. However, since this work was undertaken to solve a general problem, it did not appear profitable to attempt resolution of all individual components.

Analyses of Combustion Products

Figure 4 shows results of an analysis of combustion products of *n*-hexane obtained with a three-stage chromatograph. The chromatograms are complex, even if each peak represents only one compound, which in itself is unlikely. Small peaks may be seen in the first-stage chromatogram between 57 and 72 minutes. These peaks may represent C_4 or C_5 alcohols, C_{10} ethers, C_8 or C_9 aldehydes, or C_9 ketones. It is difficult to identify peak components in this range, and a practical solution is to include materials represented by these peaks as a part of total oxygenates. Water is eluted from the first stage in a large tailing peak beginning at about 76 minutes. Because of the size of the water peak in an analysis such as shown in Fig. 4, stage one is incapacitated for the remainder of the analysis. A sample fraction from the third stage of this chromatograph was recovered for reanalysis in the single-stage apparatus, and the chromatogram of this analysis is shown in Fig. 5. The compounds shown by this analysis are typical of oxygenates in combustion gases. Ethylene oxide and acetaldehyde constitute a relatively large fraction. The concentration of propylene oxide is small; perhaps this is because of this compound's tendency to form propionaldehyde. Acetone and acrolein are common components of exhaust prod-

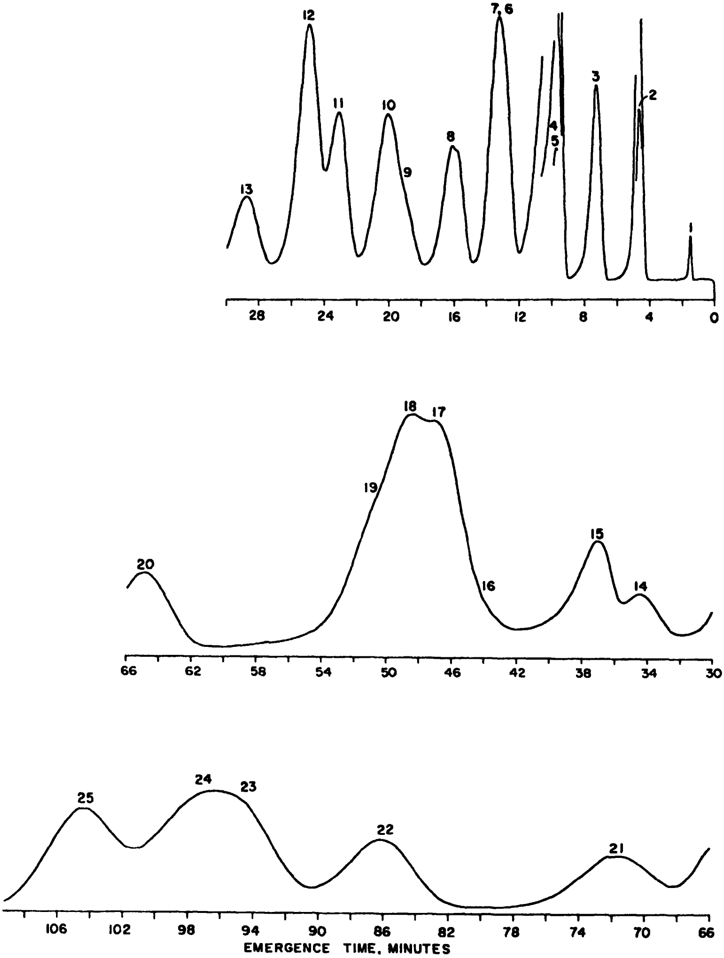

FIG 3. Separation characteristics of single-stage chromatograph. 1: air; 2: *n*-hexane; 3: isooctane; 4. acetaldehyde; 5. ethylene oxide; 6: methylal; 7: propylene oxide; 8: *n*-octane; 9. propionaldehyde; 10: 1,1-dimeoxyethane; 11: acetone; 12: acrolein; 13: diethoxymethane; 14: butyraldehyde; 15: methanol; 16: crotonaldehyde; 17: benzene; 18· ethanol, 19: 3-me-2-butanone; 20: *n*-decane; 21: 2,3-butanedione; 22: meisobutyl ketone; 23: toluene; 24: propanol; 25: isovaleraldehyde; Helium flow· 80 ml/min; temperature: 58°C.

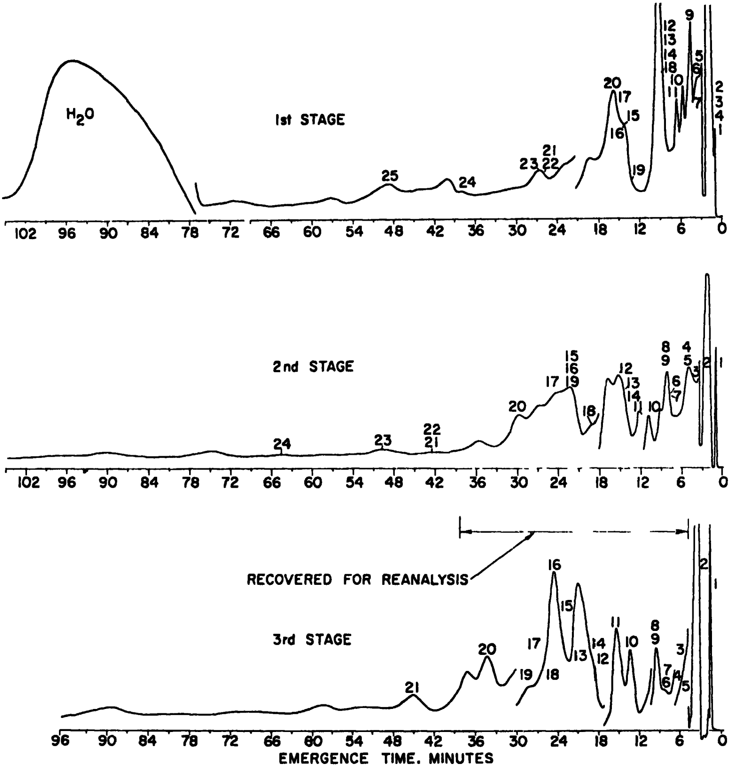

FIG 4. Chromatograms of combustion products. 1: air, CO_2, etc ; 2 *n*-hexane; 3: ethylene oxide; 4: acetaldehyde; 5: propylene oxide; 6: propionaldehyde; 7: isobutyraldehyde; 8: acetone; 9: acrolein; 10: butyraldehyde; 11: meetketone, 12. 1,2-dimeoxyethane; 13: 3-me-2-butanone; 14: 3-buten-2-one; 15: methanol; 16: isopropanol; 17: ethanol; 18: 3-pentanone; 19: 4-me-2-pentanone; 20: isovaleraldehyde; 21: propanol; 22: heptanone-3; 23: isoamylether; 24: allyl alcohol; 25: 2,4-pentanedione. Fuel: *n*-hexane; helium flow: 80 ml/min; temperature: 70°C

ucts, and acrolein, as is usual, is the larger constituent. Peak No. 11 is suspected to represent a tetrahydrofuran, but lack of calibration compounds has prevented verification. In comparing the third-stage chromatogram, Fig. 4, with Fig. 5, it may be seen that 1,2-dimethyloxyethane, isopropanol, ethanol, and 3-pentanone are identified in Fig. 4 but not Fig. 5. These and other oxygenates are believed to be obscured by the large

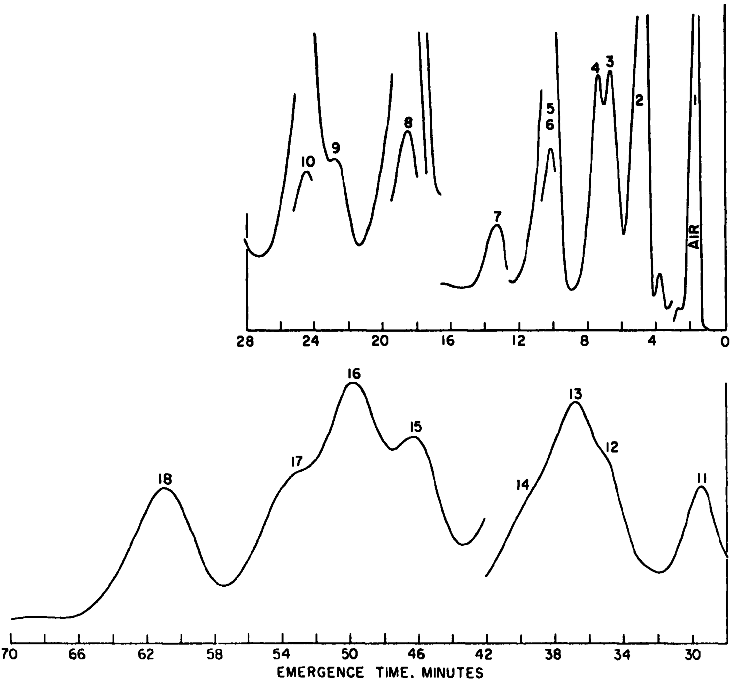

FIG 5. Reanalysis of fraction recovered from three-stage unit. 1: air; 2. *n*-hexane; 3: methylcyclopentane; 4· ethyl ether; 5: ethylene oxide; 6: acetaldehyde; 7: propylene oxide; 8: propionaldehyde; 9: acetone; 10: acrolein; 11: unknown; 12: butyraldehyde; 13: methanol; 14: methyl ethyl ketone; 15: benzene; 16: 3-methyl-2-butanone; 17: 3-buten-2-one; 18: unknown Helium flow: 80 ml/min; temperature: 58°C.

benzene and 3-methyl-2-butanone peaks shown in Fig. 5. The compounds 4-methyl-2-pentanone, *n*-propanol, and isovaleraldehyde were on the original chromatogram but were removed from Fig. 5 because the original chromatogram was too large to be reproduced conveniently.

Recovery of Fractions from Chromatographic Analyses

Gas chromatography is a powerful analytical tool, but retention-time data frequently are not sufficient for identification of components represented by chromatographic peaks. Too, chromatographic determinations of combustion products are handicapped by the lack of suitable column calibration standards. Therefore, methods for secondary identification of chromatographic fractions are necessary in this analytical problem. Both the mass spectrometer and the infrared spectroscope are useful for this purpose. For the oxygenated compounds discussed in this report, an infrared (IR) analysis is probably of more value than an analysis obtained with a mass spectrometer. However, the individual oxygenates are quantitatively small (2 to 300 μg), and this amount may be too low for an adequate IR analysis. Fractions may be recovered by a freeze-out technique, but because of the small amount of sample that is involved, extreme care must be taken to remove organic contaminants from the recovery system. A system to accomplish this is shown in Fig. 6. Prior to making a recovery, the system is evacuated at room temperature for several minutes at less than 1 μ pressure. The freeze-out loop is immersed in liquid air and dried helium is admitted until the relief valve indicates that the system pressure is slightly above atmospheric. By manipulation of the proper stopcocks, a peak fraction is bypassed through the freeze-out loop with little disturbance of the associated chromatographic detector. After a fraction is collected the trap is valved off and the recovered fraction may be transferred to the removable sample tube. This is accomplished by immersing the sample tube in liquid air and heating the freeze-out loop to approximately 212°F.

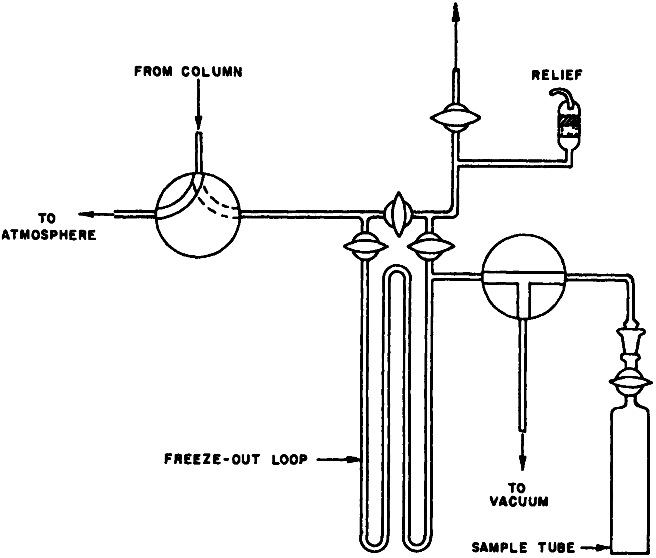

FIG. 6. System to recover fractions from chromatographic unit.

The short tubing involved makes the vapor transfer relatively simple. The samples thus recovered may be analyzed by a mass spectrometer or, if the sample is sufficiently large, it may be analyzed by infrared spectroscopy.

Limitations of Methods

The chromatographic methods and equipment that have been discussed do not apply adequately to analyses for formaldehyde, peroxides, hydroperoxides, and fatty acids. This exclusion ordinarily applies to all compounds that are unstable or which react with the column substrate.

It is generally accepted that formaldehyde is one of the more abundant oxygenates found in combustion products. However, a chromatographic identification of formaldehyde, in which the sample was either a gas or a water solution, has not been successful. Presumably, this is because formaldehyde, particularly the gas, polymerizes readily under these operating conditions. Efforts have been made using gas chromatography to separate formaldehyde as a low molecular weight polymer, but the results have not been satisfactory. Attempts also have been made to reduce formaldehyde to methanol and to analyze for the alcohol, but the degree of conversion was too low for quantitative usefulness.

The fatty acids will react with the glycol substrate and therefore cannot be introduced into the first two stages of the staged unit. The silicone column used in the third stage is adequate for the analysis of a mixture of such acids (*2*). However, in these studies there was no attempt to use the silicone column for analysis of fatty acids which may exist in combustion products.

Peroxides and hydroperoxides are considered too unstable to survive GLPC analyses, but these studies have included a few of such materials.

In the analyses of oxygenates in combustion products from a gasoline fuel, there will be chromatographic interference offered by C_{10} and higher hydrocarbons. If this problem is presented it may be met by a series of GLPC analyses, fraction recoveries, and reanalyses, but at best this is a slow and tedious procedure.

SUMMARY

Gas-liquid partition chromatography has been used to separate and identify oxygenated derivatives of hydrocarbons which are found in the products of combustion of hydrocarbon fuels. A three-stage GLPC unit is used to make a gross separation of hydrocarbons, oxygenated materials, and water; fractions that are unresolved are recovered for reanalysis in a single-stage chromatographic unit.

The general range of oxygenated compounds for which the chromatographic equipment can be used covers ethylene oxide through *n*-pentanol.

Oxygenated combustion products that have been identified by chromatographic methods are: ethyl ether, ethylene oxide, propylene oxide, acetaldehyde, propionaldehyde, acetone, acrolein, methyl ethyl ketone, *n*-butyraldehyde, 3-methyl-2-butanone, 3-buten-2-one, isovaleraldehyde, and *n*-propanol. Tentative identifications have been established for a number of other oxygenated components.

A system is described for the recovery of chromatographic fractions. The system allows the collection of a sample that is relatively free of organic contaminants, and that is in suitable form for secondary analyses by mass and infrared spectroscopy.

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CHAPTER XVIII

A Versatile Gas Chromatographic Instrument

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Duplicates of a versatile but compact gas chromatograph were built in this laboratory. They were then rebuilt to improve the ease of sampling for preparative gas chromatography and the heating of vapor transfer lines. The instruments can be and have been applied to a wide range of analytical uses as well as to preparative gas chromatography. To aid exploratory as well as final analytical and preparative operations, flexibility was stressed in flow control, gas and liquid sampling, column handling and heating, and collection of isolated components.

Any of four independent flow rates is immediately available by opening a toggle valve. Gases either above or below atmospheric pressure can be sampled into either one or two accessible and interchangeable reservoirs from 2 to 500 ml in volume; the pressure in these reservoirs can be measured; and the contents of the reservoirs can be charged separately or together to the columns.

Three columns are usable in series or singly at any time. The columns are easily installed and removed. The columns or sections of columns can be heated separately. These features allow the analysis of mixtures of vapors and permanent gases by the combination of gas-solid and gas-liquid chromatographic columns and the rapid analysis of mixtures of wide boiling range by temperature programming of columns.

Careful provision has been made for components separated in preparative gas chromatography. These proceed to any of four selectable ports through evenly heated lines of known temperature either with or without contact with the detector, at the option of the operator. Additional heated lines attached to the ports carry the components to receivers designated to eliminate fogging and to be flexible in application.

This paper is a progress report on this instrument and a description of certain of its applications. The instrument is simple, compact, capable of being put together in the average laboratory, and unusually flexible in application.

DESCRIPTION OF THE INSTRUMENT

Two replicates of the present instrument have been made. One has been mounted on a stationary rod frame, as shown by front and rear views in

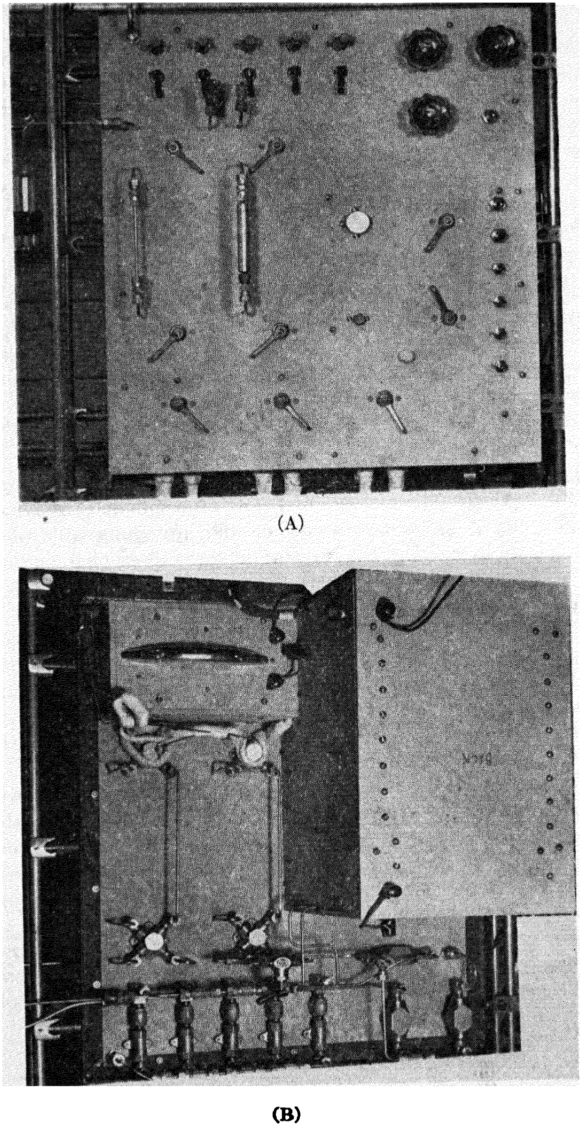

Fig. 1. Frame-mounted gas chromatograph. (A) Front view; (B) rear view.

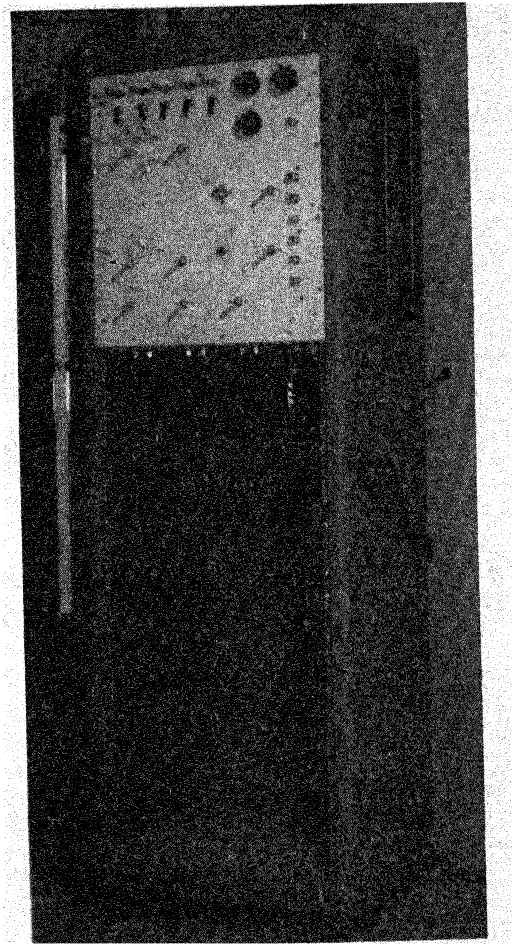

FIG. 2. Gas chromatograph mounted in standard relay rack.

Fig. 1; the other has been mounted in a standard relay rack, as shown in Fig. 2. The frame-mounted instrument can, after release of a wing bolt and three quick-connects, be quickly and easily exposed for alteration or servicing by rotating it around a vertical aluminum rod in the plane and to the left of the face. Another rod, the bottom of which rests on the laboratory floor, supports the right side of the instrument. The rack-mounted instrument is accessible through the rear door of the relay rack.

The facing panel of the instrument is 19 inches wide, 21 inches high, and, like the other panels, is made of ¼-inch Transite. The face is mounted on and reinforced by a 1-inch angle iron frame. On the face are mounted the tubing and valves for flow control, sampling, and collection of chromatographed components. Behind the face are the ovens.

The large and small ovens which are supported from and extend back from the face enclose the hot-wire thermal conductivity detector and all tubes and valves which carry condensible vapors, except for a 6-inch optionally heated part of the sample injection line. Each side of the ovens carries its own heating ribbon, outside terminal posts for the ribbon, and brackets for attachement to neighboring sides. The quantity and/or distribution of heat within the ovens can, therefore, be easily changed. Also, the ovens can be dismantled one side at a time, facilitating servicing and rerouting of tubing within the oven as required.

The gas flow diagram is given in Fig. 3, which shows one possible direction of gas flow for preparative gas chromatography and the facilities within the instrument for flow control, sampling, detection, collection of components, and flow measurement. The carrier gas enters via a ¼-inch bulkhead union in the instrument face and is manifolded to five needle and toggle valve combinations. Four of these, S1-S6, S2-S7, S3-S8, and S4-S9, provide four independent, selectable flow rates; the other, S5-S10, provides a controlled flow of gas to the reference side of the detector. (The needle valves are made by Ideal-Aerosmith, Inc., Hawthorne, California; the toggle valves by the Hoke Co., Cresskill, New Jersey.)

The carrier gas then flows through four-way reversing valve S23 to and through the following sampling facilities: micropipette sampling port C, syringe injection sampling port D, and reservoir charging valves S18 and S17. With these and with valves S15 and S16, analytical and preparative liquid and gas sampling can be accomplished.

Liquid sampling for analytical gas chromatography can be accomplished by micropipette injection at port C or by syringe injection at port D. The micropipettes can furnish samples from 10^{-3} to 10^{3} μl and are available from the Precision Instrument Co., Baton Rouge, Louisiana. An improved micropipette charging assembly has been developed which requires only a two-way ⅜-inch Republic Teflon plug valve. This assembly assures positive sample charging, one-way flow of gas, and results which are independent of operator technique. The details are shown in Figs. 4 and 5. The sample line from port C through to valve S19 is separately and variably heated, and is monitored by four thermocouples.

In sampling gases for analytical gas chromatography, the gas reservoirs

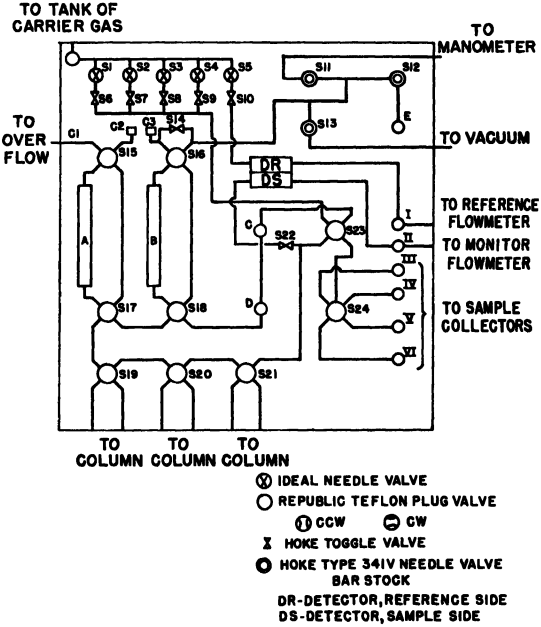

FIG 3. Flow diagram: gas chromatograph

A and B and the connecting lines can be evacuated by opening S13 to vacuum; pressures can be measured by opening S11 to the manometer (valves S11, S12, and S13 are Hoke Type 341 Bar Stock Needle Valves). The reservoirs A and B are contained between valves S16 and S18, and S15 and S17, respectively. Reservoir B, if previously evacuated, can be filled with gas by placing valve S16 counterclockwise (CCW), S18 clockwise (CW), opening toggle valve S14, and closing connection C3 with a plug—connections C2 and C3 are ⅛-inch tubing unions located in front of the face of the instrument. Once filled to the desired pressure, reservoir B is closed by turning S16 CW. The gas in reservoir B can then be charged to the columns by turning S18 CCW for a few seconds; the carrier gas coming from sample port D is diverted through S16 and reservoir B, moving the sample before it. After the sample has been charged, valve S18 is returned CW.

If gas sampling by flushing the reservoir is desired, connection C3 can be left open, toggle valve S14 closed. The gas sample then flows from S16 to

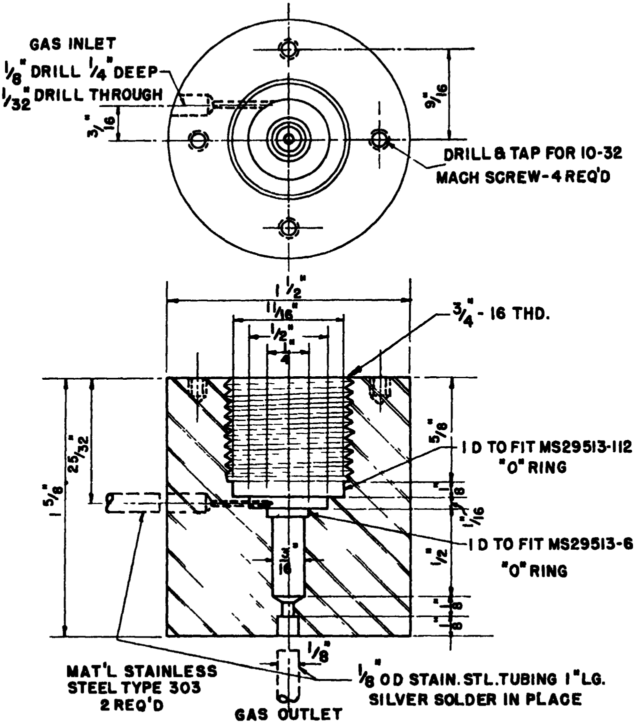

FIG 4 Micropipette sampling port

S18, through reservoir B, and out connection C3. The gas sample can be stored and then charged to the columns as described in the preceding paragraph.

Reservoir A as well as B can be used by connecting C2 and C3. A sample can then be stored in one reservoir, an internal standard in the other; the two can be charged either simultaneously or sequentially.

Reservoirs A and B are each 4 inches long and terminate in 1/8-inch unions. The vertical axes of the reservoirs and the 1/8-inch unions are 2 1/8 inch in front of the instrument face. Thus, interchangeable reservoirs giving total sample volumes from about 2 ml to about 500 ml are available and easily installed.

Liquid sampling for preparative gas chromatography is accomplished by turning valves S15 CCW, S17 CW, and by injecting a sample through a

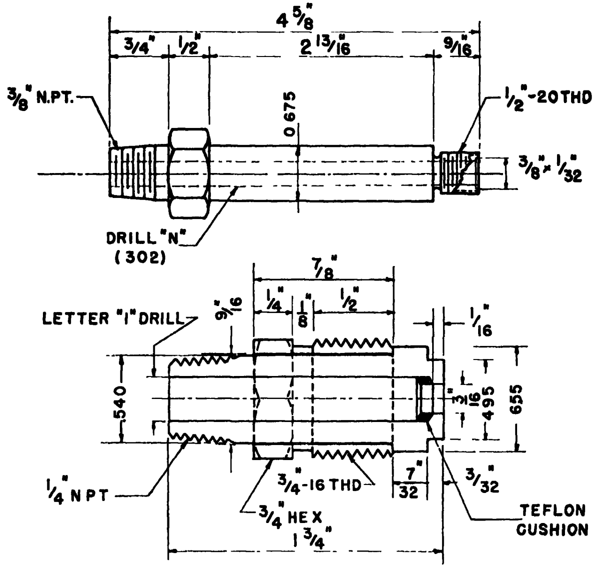

FIG. 5. Micropipette sampling accessory adapters for Republic Valve 309-GG-3/8 inch ST STL

septum at connection C2 until overflow is seen at connection C1. The overflow shows that the right line from S15 to S17 and the left line—reservoir A—are filled. The same method is used for charging gas samples and these large liquid samples: S15 is turned CW, then S17 CCW. The carrier gas thus enters reservoir A from the top and the liquid sample drains and is pushed through S17 and S19 into the column or columns. The liquid sampling system can be cleaned by injecting solvent at C2, then diverting the carrier gas through reservoir A and associated tubing by connecting C2 and C3, plugging the top union leading to reservoir B, opening toggle valve S14 (S11, S12, S13 closed) and turning S18 CCW and S16 CW.

After passing through the sampling facilities, the carrier gas proceeds through column valves S19, S20, and S21. To each valve a column can be attached. The carrier gas can be directed into (CCW) or past (CW) any column at any time, so that multicolumn operations can be carried out. The direction of gas flow from valve S21 depends on whether the gas chromatrographic operation is preparative or analytical.

In preparative gas chromatography, the tubing can be arranged as shown in Fig. 3 to carry just part of the gas stream through the detector. In this case, the gas stream flows from S21 to a *T*; part—about 20 ml/min—flows from the *T* through the detector to port II for flow measurement. Most of the gas stream flows from the *T* through Ideal-Aerosmith needle valve S22 which regulates the proportion of the stream diverted to the detector. Valve S22 is adjustable by screw driver through a normally closed hole in the face of the instrument. After leaving S22, the bulk of the gas stream flows through S23 to distribution valve S24 and finally to one of four ⅛-inch bulkhead union collection ports III, IV, V, or VI. (Valves S15, S16, S17, S18, S19, S20, S21, S23, and S24 have Teflon plugs and are made by the Republic Valve Co., 15655 Brookpark Road, Cleveland, Ohio.)

Alternatively, in preparative gas chromatography, if 100% collection of components is desired, the tubing can be arranged to carry the whole gas stream from S21 through the detector, through valve S23, to distribution valve S24, and again to one of the collection ports III, IV, V, or VI.

In preparative gas chromatography, the vaporized and chromatographed components in the carrier gas are led in individually heated and temperature-monitored ⅛-inch tubes to receivers. The result of considerable development, the receiver illustrated in Fig. 6 eliminates fogging, provides a

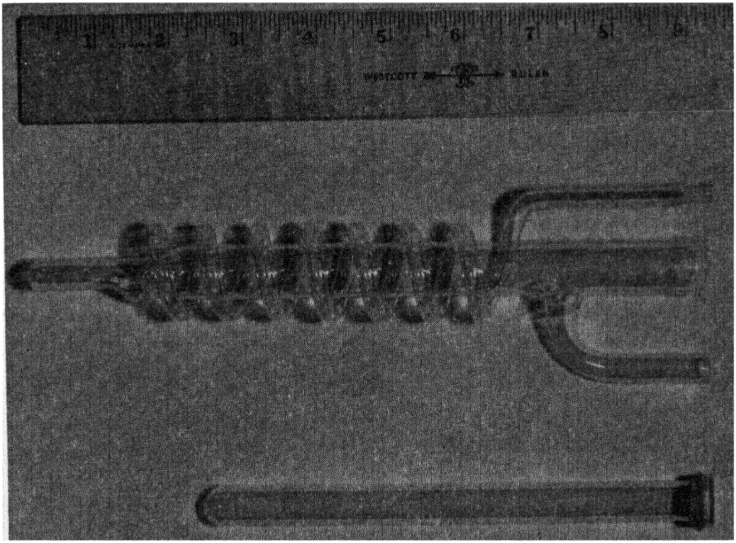

Fig. 6. Receiver for preparative gas chromatography.

needed reservoir in which the collected sample does not impede carrier gas flow and from which the sample can be easily removed, and permits flow measurement of the carrier gas. The gas enters the receiver at the slightly flared top of the helix to which the ⅛-inch tubing is sealed by a silicone O-ring. The gas is cooled gradually by the air-cooled helix and then by the water- or Dry Ice-cooled cold finger, which is sealed to the slightly flared body of the receiver by a rubber gasket cut from rubber tubing. The gas then passes out the side arm for flow measurement.

In analytical gas chromatography, the whole gas stream proceeds directly from valve S21 to the detector, then either directly to bulkhead union port II for flow measurement or through reversing valve S23 to port II, depending on whether reversal is desired.

The various pieces of ⅛-inch tubing needed for the alternative gas routes which have been mentioned are preformed and kept at hand for use as desired. An alternative route can be set up in 20 minutes.

The electrical services to the instrument include twelve ¾ kva Powerstats mounted in a radio relay rack along with the recorder and bridge circuitry, which is standard. These Powerstats permit rapidly variable heating of the columns and of column sections, as well as of the oven, detector, and sample injection points and lines. The individually wrapped columns can be given temperature gradients both along the column and in time, and yet quickly regain initially low starting temperatures, thus facilitating the processing of successive samples. The use of these temperature gradients will be illustrated more fully under *Applications*.

The body of the Gow-Mac hot wire detector has been altered to give direct flow over the elements on the sample side. The resultant positive cleaning of the detector eliminates tailing caused by slow diffusion away from the detector elements, but it limits the flow rate to about 300 ml/min and also makes the detector sensitive to small pressure changes in the laboratory. This sensitivity can be overcome and a satisfactory base line obtained by passing the effluent gas through about 50 ft of ¼-inch OD Tygon tubing. The detector and, in preparative work, the lines leading to it are separately wrapped and heated, so that the base line shows little evidence of variable column heating.

The signal attenuator and the recorder again emphasize flexibility. The signal can be attenuated in two ways: in 5 divisions, each by a factor of 4, over a range of 1024, for survey work; or in 20 divisions, over the same range, for analytical work. The Brown recorder has a sensitivity of 1 mv, full-scale deflection of 1 sec, and is equipped with an Insco chart speed changer, allowing almost instant selection of any one of eight chart speeds, from ¾ to 24 inches per hour.

APPLICATIONS

Supplanting a Spinning-Band Distillation

The literature on preparative gas chromatography (*1–4*) has described excellent but rather lengthy separations. The potential speed and flexibility of the method have not been emphasized. We cite a case from our laboratories in which a large number of samples, each comprising a series of even-numbered carbon alkenes plus normal heptane, required spinning-band distillation. The isomeric cuts were to undergo infrared analysis. A gas chromatographic fractionation was proposed to supplant the distillation.

The gas chromatographic fractionation was to yield cuts with a minimum volume of 0.1 ml amounting to as little as 1% of the total sample. The fractionation was to be completed within an hour. The cuts, once obtained, would then require no special microtechniques for infrared analysis; and the fractionation would be about ten times faster than spinning-band distillation. The fractionation of the C_4–C_{10} sample, necessarily 10 ml in size (1% of 10 ml = 0.1 ml), was accomplished by suitable choice of column and of operating procedures.

Three ⅜-inch OD columns, the first 3 ft long, the second 9 ft long, and the third 18 ft long, were packed with 20 wt % Dow Corning Silicone High Vacuum Grease deposited from a benzene suspension onto 30 60 mesh Columpak (Fisher Scientific Co.). A separate heater winding was applied to each column.

Preliminary studies established the times of passage of components through the columns. With this information, the following operating procedures were developed. The sample was syringe-injected into heated inlet lines and carried into all columns, with the first column at 135°C, the second at 80°C, and the third at 25°C. Flow rate through all columns in series was 960 ml N_2/min. Application of successive prescribed changes in flow direction and column temperature was indicated by returns of the recorder pen to the base line, showing successive completions of fraction collection. The pattern of changes is given in Table I.

A typical record is shown in Fig. 7. The sharp returns to the base line showed clearly that a fraction had been collected and that the next change of conditions was in order.

The cuts from the many samples fractionated, at one hour per sample, were large enough to require no special skill in handling and were not detectably contaminated by neighboring cuts. They were, however, occasionally contaminated by traces of the silicone stationary phase but not badly enough to interfere with the infrared analysis. In this application, preparative gas chromatography was faster, more reliable, and more efficient than alternative methods of separation. Because the method was easy

TABLE I

OPERATING PROCEDURE FOR ALKENE FRACTIONATION BY GAS CHROMATOGRAPHY

Event	Minutes elapsed	Columns in use			Temperatures, °C		
		First	Second	Third	First	Second	Third
Inject sample	0	x	x	x	135	80	Room
After C_4 collection	5	x	x	x	135	80	35
After C_4 collection	18			x			35
After C_6 collection	20			x			60
After nC_7 collection	35			x			120
After C_8 collection	50	x	x		135	135	—

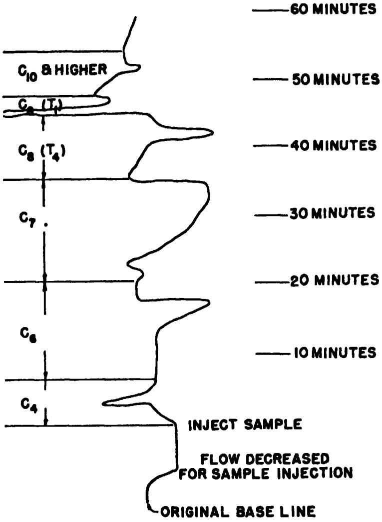

FIG. 7. Gas chromatographic fractionation of hydrocarbon mixture having wide boiling range. Tracing of strip chart record.

and fast, samples rarely required refractionation. Finally, the relatively low temperatures of the gas chromatographic approach help protect possible labile components such as were at hand.

The application just cited was carried out on the predecessor of the instrument described here. This routine use of this predecessor showed the need for easier sampling and for more uniform heating. Samples were then charged by direct syringe injection against pressure. This was difficult, sometimes dangerous, and limited the sample size to 10 ml. Samples are now charged in an easy two-step procedure which has been described, and a wide and easily usable variety of sample sizes are available. Vapor transfer also needed improvement.

That just wrapping vapor transfer lines with heating tape does not overcome condensation was repeatedly demonstrated. The successful remedy adopted is enclosure of these lines in an oven, with heating elements not only on the sides of the oven but also tracing out the critical lines.

SEPARATION OF THREE C_8 ISOMERIC CHLORIDES

A successful and useful application of the present instrument was the separation of three C_8 isomeric chlorides. Infrared examination of the separated isomers would allow correlation of a given chromatographic peak with a given isomer. Distillation had failed to make the separation. Attempts with a commercial instrument to conduct a preparative gas chromatographic separation with ordinary microliter samples had repeatedly failed either to make a complete separation or to yield enough material to be usable by the infrared laboratory. What had been prepared was inexplicably and grossly contaminated. The results from the successful macroscale separation to be described explained this contamination.

The separation of a 2.5-ml sample was accomplished by proper choice of column, stationary phase, and operation procedure. Three separately and variably heated 16 ft by ½-inch OD columns were packed with 30 wt % β,β'-iminodipropionitrile on 30–60 mesh Columpak. The columns were used in series. The temperature of the first column was 105°C; of the second, 75°C; and of the third, 40°C. These temperatures were constant during the fractionation.

The carrier gas flow was 590 ml/min, of which 25 ml/min or about 4% was passed through the detector. The fractionation took about 2½ hours. The recorder trace is reproduced in Fig. 8. (The sharp break at about 100 minutes was caused by shutting off the gas, recorder, and column heaters overnight and turning them on again the next morning.)

Infrared spectroscopic examination of the collected fractions showed complete separation of the isomers. Although each fraction contained a detectable but negligible trace of the stationary phase, this could, if necessary, have been removed by vacuum transfer of the isomer. The identification of the isomers with the corresponding chromatographic peaks was immediate.

Analytical gas chromatographic examination of the fractions (60 ft of 5 wt % β,β'-iminodipropionitrile in a ¼ inch OD column at 132°C; 60 ml He/min) showed a trace contaminant in increasing amounts in the succes-

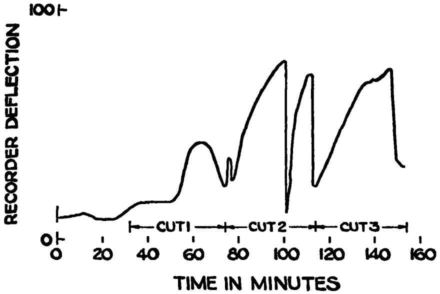

FIG. 8. Preparative gas chromatographic separation of three isomeric chlorides

Sample size: 2.5 ml; stationary phase; B,B'-iminodipropionitrite; column dimension: 48 ft by ½-inch OD; temperature of first 16-ft column was 105°C, of the second 16-ft column, 75°C, and of the third 16-ft column, 40°C; flow rate 565 ml N_2 per min.

sively collected fractions. Although the β,β'-iminodipropionitrile obviously could separate the contaminant from each isomer, the contaminant was present in each separated isomer in an amount proportional to residence time in the columns. The contaminant must, therefore, have been a product of thermal degradation taking place not in the vapor transfer lines but in the columns. Some of the contamination of the earlier microscale work is thus partially explained.

Those earlier products from a commercial instrument apparently had not only been considerably degraded but had also condensed in the exposed bulkhead union which was not directly heated. (Another commercial instrument has for product collection a considerable length of unheated exit tubing plus an unheated exit valve. These can easily condense and thus contaminate all products of low volatility after the first one collected.) The earlier collected products were thus a mixture of thermally degraded materials and a number of previous line condensates. The importance of keeping the complete length of the vapor transfer lines adequately hot is thus again demonstrated.

ANALYTICAL CAPABILITY

The analytical capability of the instrument is demonstrated in Fig. 9, showing partial resolution of an arbitrary mixture of C_5 olefins. The 60-ft column used contained 5 wt % acetonyl acetone on Columpak. Calculated on the basis of the 2-methyl-2-butene peak, base width 4 mm, retention 133 mm, this column and the detection system show a separation corresponding to about 18000 theoretical plates. Such resolution is adequate for most analytical purposes, given a suitable stationary phase. (A 30-ft col-

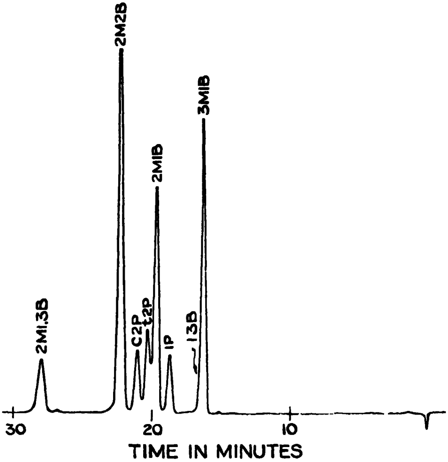

FIG. 9 Demonstrative 18000-plate partial separation of hydrocarbons by gas chromatograph

Column: 60 ft by ¼-inch OD; stationary phase: 5 wt % acetonylacetone; support Columnpak. 30–60 mesh; temperature. 25°C; flow rate: 43 ml HC per min; sample size: 1 μl.

KEY 3M1B: 3-methyl-1-butene, 1,3B: 1,3-butadiene, 1P. 1-pentene; 2M1B: 2-methyl-1-butene, t2P. *trans*-2-pentene; c2P· *cis*-2-pentene; 2M2B: 2-methyl-2-butene; 2M1,3B· 2-methyl-1,3-butadiene

umn containing 10 wt % safrole on Columpak completely resolves the mixture cited in Fig. 7.)

SUMMARY

Duplicates of a versatile, compact gas chromatograph have been built and described which have unusual flexibility for flow control, gas and liquid sampling, column handling and heating, and collection of chromatographically separated components. Preparative fractionations of a 10-ml sample of a wide-boiling-range hydrocarbon mixture within an hour and of a 2.5 ml sample of three isomers are described. A separation corresponding to 18000 theoretical plates has been cited to demonstrate the analytical capability of the instrument.

ACKNOWLEDGMENT

The many helpful suggestions and fine work of Lester M. Morse, who assembled the instrument, are sincerely acknowledged.

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CHAPTER XIX

Automatic Fraction Collector for Gas Chromatography

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It is widely acknowledged that the collection of individual fractions from a gas chromatographic column is highly desirable, since fractions can then be identified by infrared absorption, specific reagents (*1*), or other methods. So far we have been unable to find a commercial fraction collector that can free the operator from the time-consuming task of collecting samples manually. We therefore decided to build an automatic fraction collector that meets our requirements. In our opinion an automatic sampler must be reliable and require a minimum of attention and maintenance. Since laboratory funds as a rule are far from unlimited, the cost of such an instrument has to be kept within reasonable bounds. We feel that our instrument is a satisfactory solution of our problem and can hardly be surpassed as far as reliability and simplicity is concerned.

MECHANICAL CONSTRUCTION

The mechanical portion of the instrument consists of a center post of brass, tapered at the top. On this tapered portion rides a brass ring, which in turn carries a brass cylinder. The lower portion has a large gear attached and is held in place by a ball bearing. This assembly has channels drilled to give twelve sample stations and also a bypass to prevent excessive back pressure in the column during switching (Fig. 1). The twelve outlets are fitted with hypodermic needles which in turn reach down into the receivers held by clamps (Fig. 2). The receivers are made from 2-mm capillary borosilicate glass tubing. Note the wider portion near the top which prevents spilling of the liquid (Fig 3).

CONTROL SYSTEM

In order to supply the collector with a signal to change receivers, several methods are possible. The recorder can be equipped with a retransmitting slide-wire feeding a discriminator circuit that can detect the start and end of a peak. This approach was quickly dropped since the electronic circuit can hardly be called simple and inexpensive. For the same reasons an integrating circuit was found not suitable. One might install a microswitch in the recorder near the zero mark much like a limit switch. This, however,

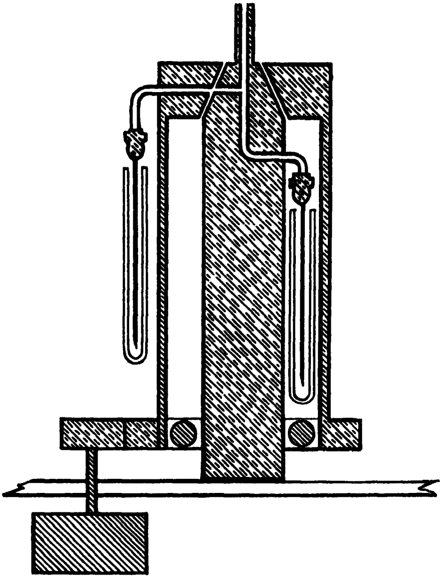

FIG 1. Automatic fraction collector.

will introduce objectionable drag on the servo system near the base line. We do not like to tie up a recorder for one specific job only, so this again is not a desirable solution. A light-operated switch was finally chosen, since the cadmium sulfide crystal cells* available today, are only ¼ inch in diameter and about ¾ inch long. These small dimensions make the mounting of the photocell in the recorder a rather simple task. Only a small hole has to be drilled in the recorder frame above the gear train, in which the cell is held by a rubber grommet (Fig. 4). A small strip of aluminum foil clipped to the pen carriage shields the photocell from the light of the built-in illumination of the recorder.

The photocell is connected to a thyratron switch by a shielded cable. The thyratron switch consists basically of a 2D21 tube, a Potter and Brumfield plate circuit relay, type KCP 11, 2500 ohms, a PB relay KRP14A, 115 volts 60-cycles, and a power transformer 25 va, 120 volts at 100 ma secondary. The wiring diagram is illustrated in Fig. 5. The CdS cell is a resistive element whose resistance decreases under increasing illumination.

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* Clairex Corporation, New York, New York.

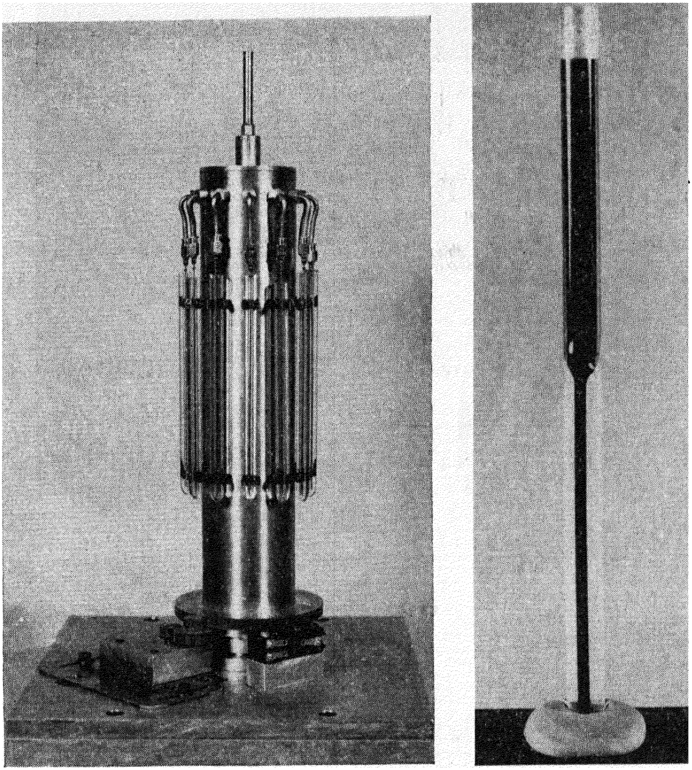


FIG. 2. FIG. 3.

FIGS. 2 AND 3. Automatic fraction collectors.

This effect is used to control the thyratron tube. In the plate circuit a normally closed relay, bypassed by a 1-μf condenser to prevent chattering, controls a power relay which starts the collector motor as soon as light falls on the cell at the beginning of the peak. When the limit switch at the drum closes, the power relay is de-energized, and the limit switch can turn off the motor at the end of the required travel.

The unit is constructed on a 5 × 7 × 2 chassis with the switches, pilot lights, and sensitivity control mounted at the front.

The complete fraction collector is mounted in a relay cabinet 42 inches

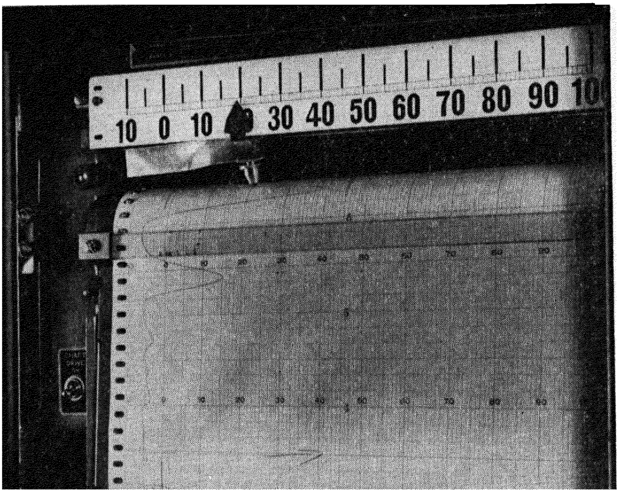
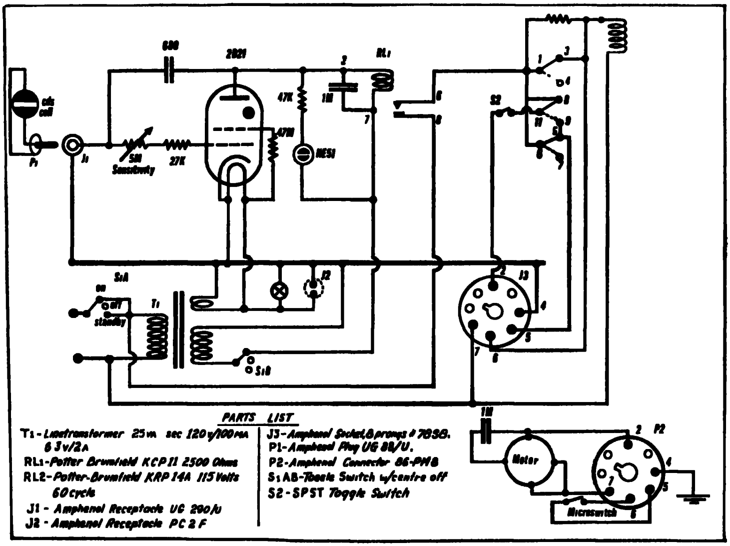


Fig. 4. Automatic fraction collector.



PARTS LIST

T1 - Linetransformer 25VA sec 120v/100MA 6 3v/2A
RL1 - Potter Brumfield KCP 11 2500 Ohms
RL2 - Potter-Brumfield KRP 14A 115 Volts 60 cycle
J1 - Amphenol Receptacle UG 290/U
J2 - Amphenol Receptacle PC 2 F
J3 - Amphenol Socket, 8 prongs # 78S8.
P1 - Amphenol Plug UG 88/U.
P2 - Amphenol Connector 86-PM8
S1 AB - Toggle Switch w/centre off
S2 - SPST Toggle Switch

Fig. 5. Automatic fraction collector.

high, with the control box mounted on the left side, and the recorder on top (Fig. 6). This makes a neat and compact installation.

The Perkin-Elmer Vapor Fractometer Model 154 was turned 90° (as shown) and the pipe connection from the detector shortened to the very minimum in order to reduce the time lag between indication from the detector and arrival at the collector (Fig. 7).

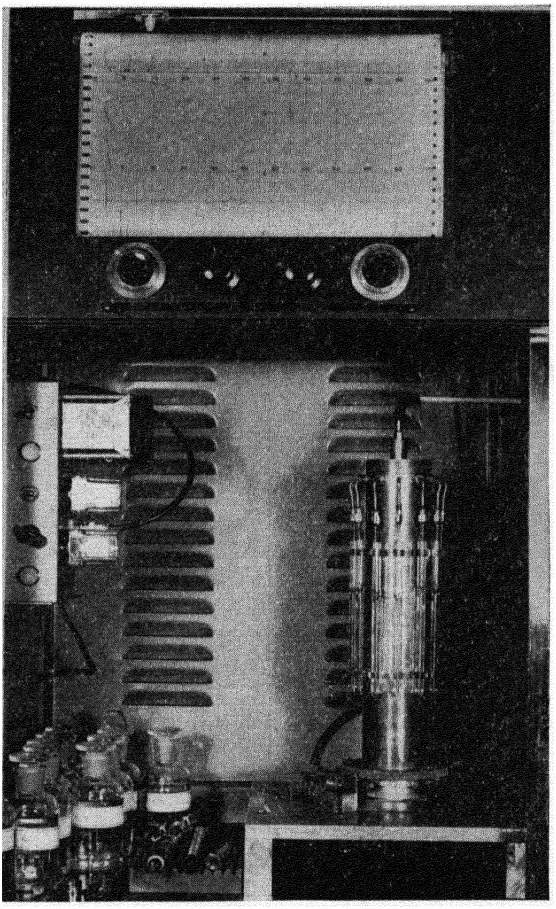


FIG. 6. Automatic fraction collector.

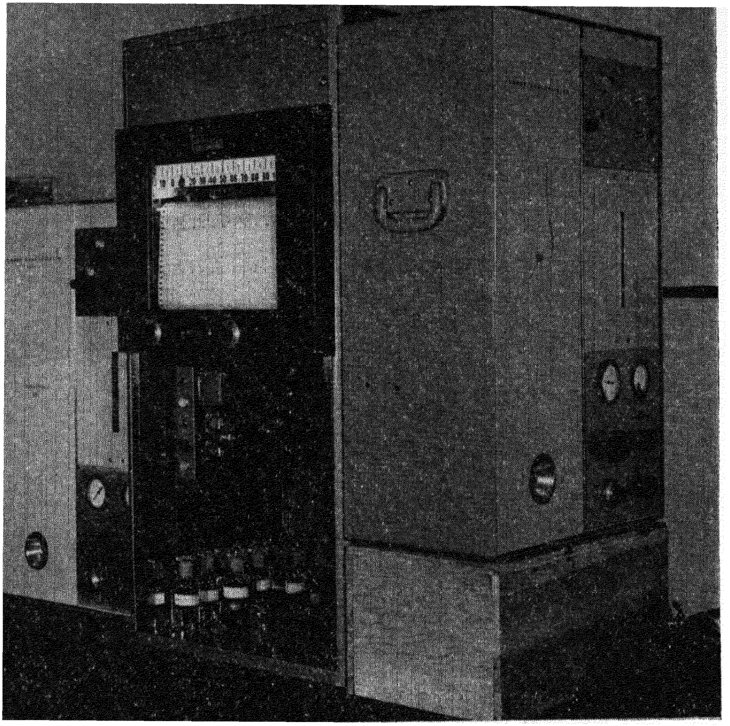


Fig. 7. Automatic fraction collector.

PERFORMANCE

The unit has been used to collect fractions from synthetic mixtures of commonly encountered organic solvents. These were prepared as two component mixtures 50/50 by volume. Column temperature was 80°C; column material, diisodecyl phthalate; helium pressure, 10 psig; and sample volume injected, 10 μl. Specific group reagents for aromatic hydrocarbons, ketones, and alcohols were placed in the receivers. This data is tabulated in Table I.

In Table I above please note that each horizontal entry lists the positive or negative response obtained with one group reagent. Thus in line 1 two consecutive receivers contained the aromatic reagent, and a positive response was given in the second receiver, corresponding to the benzene peak. The test materials contained an aromatic hydrocarbon, aliphatic

TABLE I

Mixture	Reagent	Receiver 1	Receiver 2
Acetone-benzene	Aromatic	Negative	Positive
Acetone-benzene	Ketone	Positive	Negative
Acetone-benzene	Alcohol	Negative	Negative
Acetone-cyclohexane	Aromatic	Negative	Negative
Acetone-cyclohexane	Ketone	Positive	Negative
Acetone-cyclohexane	Alcohol	Negative	Negative
n-Hexane-benzene	Aromatic	Negative	Positive
n-Hexane-benzene	Ketone	Negative	Negative
n-Hexane-benzene	Alcohol	Negative	Negative
Isooctane-benzene	Aromatic	Negative	Positive
Isooctane-benzene	Ketone	Negative	Negative
Isooctane-benzene	Alcohol	Negative	Negative
Methylene chloride-benzene	Aromatic	Negative	Positive
Methylene chloride-benzene	Ketone	Negative	Negative
Methylene chloride-benzene	Alcohol	Negative	Negative
Methanol-benzene	Aromatic	Negative	Positive
Methanol-benzene	Ketone	Negative	Negative
Methanol-benzene	Alcohol	Positive	Negative
Ethanol-benzene	Aromatic	Negative	Positive
Ethanol-benzene	Ketone	Negative	Negative
Ethanol-benzene	Alcohol	Positive	Negative
Methyl acetate-benzene	Aromatic	Negative	Positive
Methyl acetate-benzene	Ketone	Negative	Negative
Methyl acetate-benzene	Alcohol	Negative	Negative
Ethyl acetate-benzene	Aromatic	Negative	Positive
Ethyl acetate-benzene	Ketone	Negative	Negative
Ethyl acetate-benzene	Alcohol	Negative	Negative

hydrocarbons, cyclohexane, two aliphatic esters, two aliphatic alcohols, acetone, and methylene chloride. From this group of test material no false positive tests were obtained, confirming the correct performance of the collector.

The use of such a fraction collector together with a group reagent test procedure should be of great assistance to organic and analytical chemists. It should help infrared identification, since all that is necessary is to be able to collect enough of the desired components in appropriate receivers.

Obvious modifications of technique and apparatus suggest themselves such as the use of two-stage receivers in each collecting position, or collection by freeze-out rather than in a solvent or reagent solution.

SUMMARY

This paper described an automatic fraction collector for gas chromatography. The collector consists of a revolving drum having 12 sample positions. A simple photoelectric switch in connection with the recorder supplies the "change" signal for the motor. This combination results in a reliable yet simple instrument.

ACKNOWLEDGMENT

The author is indebted to J. L. Monkman and L. Dubois for helpful suggestions and assistance in testing the instrument.

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CHAPTER XX

Selected Applications with a New Preparative Gas Chromatograph

T. JOHNS, M. R. BURNELL, AND D. W. CARLE

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INTRODUCTION

In the first paper on gas-liquid chromatography, James and Martin (*6*) demonstrated a new technique based on the molecular separation and consequent microestimation of volatile materials. Since then an unparalleled, continuing effort has been directed toward improvement of the method for microestimation or quantitative analysis with extremely small samples. The development of very sensitive ionization detectors permits the use of microsampling which in turn improves the operation of conventional columns and makes possible the use of capillary columns (*3, 4, 5, 7, 8, 10, 11*). These new developments offer additional promise that gas-liquid chromatography can be used for a quantitative analysis with a micro amount of virtually any volatile material. However, the use of micro size samples is inconsistent with an equally important ability of gas chromatography, i.e., the separation and recovery of practical amounts of pure compounds from complex mixtures.

This feature of gas chromatography is especially interesting to the chemist who has the difficult task of separating complex organic mixtures. As compared to classical methods preparative gas-liquid chromatography can give higher separation efficiency, separation specific to compound type as well as freedom from complications such as azeotrope formation. However, if the separation ability of gas chromatography is to be useful for the preparation of pure compounds in practical amounts, it is necessary to use multigram samples. Since the capacity of conventional columns is limited to milligram quantities by the column cross-sectional area, separation of multigram samples requires a corresponding scale-up in column cross-sectional area.

It is generally agreed that scaling-up the column diameter with a corresponding scale-up in sample size results in some loss in column efficiency. The results of a study carried out in this laboratory showed that this loss is negligible up to a column diameter of about 0.7 inches. At column diameters above about 0.7 inches the rate of decrease in column efficiency increases rapidly and at a column diameter of 2 inches which

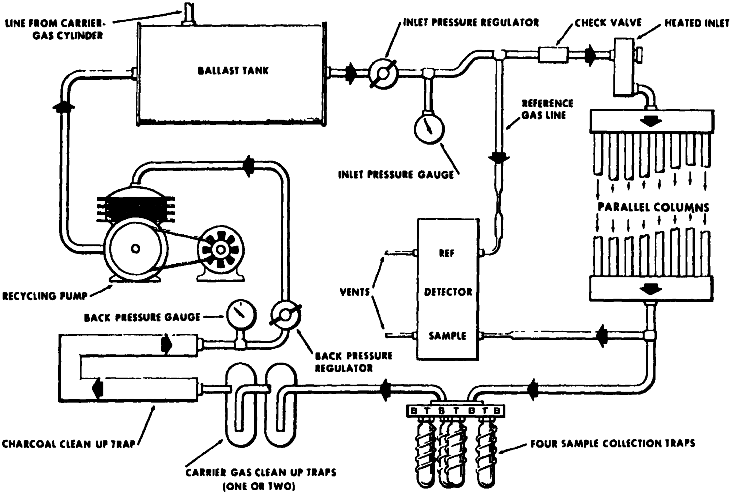

FIG 1. Megachrom flow system.

is approximately a 100-fold scale-up of a typical ¼-inch column, the HETP is increased by a factor of 4 to 5 with a column 6 ft long (*1*, *2*). A 100-fold scale-up of the size sample normally handled with a standard ¼-inch column provides practical amounts of purified fractions for most purposes such as mass spectrometer, ultraviolet and infrared analyses, micro boiling points, melting points, specific gravities and reaction studies.

The Megachrom* preparative gas chromatograph described here was designed to give a 100-fold scale-up in sample size without the serious loss in column efficiency which results in scaling-up a single column to the required diameter.

INSTRUMENT DESIGN

This instrument employs a recycle system for the carrier gas, parallel columns of ⅝ inch ID, a fraction collection valve with traps, and a system of carrier gas clean-up traps, as shown in Fig. 1. Carrier gas is introduced under pressure into the ballast tank which serves as a reservoir and a buffer volume. From the ballast tank the carrier gas flows through the inlet pressure regulator which sets the pressure at the head of the column and the flow through a pair of restrictors to the reference side of the detector. Flow through the reference side of the detector is of the

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order of 25–50 ml/min and represents about one half of the total loss of carrier gas when the instrument is operated in recycle position. Most of the carrier gas from the inlet pressure regulator is passed through the sample inlet. The sample inlet is operative at any desired temperature over the range of ambient to 450°C. It is a low thermal mass, high wattage-type vaporizer which is thermostatically controlled and maintains temperature at the desired level even during vaporization of the sample. Supply of heat on demand at a controlled temperature permits vaporization of samples with a minimum of decomposition. The carrier gas with the vaporized sample moves from the sample inlet through a heated line, which is maintained at or above column temperature, through a manifold system which distributes the carrier gas and sample equally between a series of parallel columns. At the exit end of the parallel columns the carrier gas and eluted sample are recombined with a second manifold and passed through a heated line to the fraction collection valve which is also maintained at or above column temperature. The line to this valve contains a take-off point for flow through a restrictor to the sample side of the detector. From the fraction collector valve the carrier gas which may contain bypassed sample components is put through a system of clean-up traps and then through a back pressure regulator which maintains the desired pressure at the exit end of the column and controls the flow through the sample side of the detector. From the back-pressure regulator the carrier gas moves through the recycle pump and is returned under pressure to the ballast tank. Total carrier gas flow through the instrument may be varied over the range of approximately 0.5 to 15 liters per minute of which 50 to 100 ml per minute are exhausted to the atmosphere through the detector.

The recycle pump, ballast tank, and the column package are shown in Fig. 2. The column package normally contains eight U-shaped, matched ⅝-inch ID columns 6 ft long in a unique parallel arrangement. Paralleling columns makes it possible to increase the effective cross-sectional area without using columns of excessive diameter. Over-all column efficiency of the parallel column package is approximately the same as the efficiency which would be obtained with a single column. The manifold system is designed so that by simply selecting different manifolds the column package can be changed from eight 6-ft columns in parallel to four 12-ft columns in parallel, two 24-ft columns in parallel or a single 48-ft column. Equal flow rates through the columns are accomplished by carefully balancing the pressure drop of each column and equal partitioning by filling each column with the same amount of coated packing and by maintaining each column at the same temperature. Equal temperature is maintained by mounting the columns side-by-side between two thick aluminum plates machined so that each column is encased by the alu-

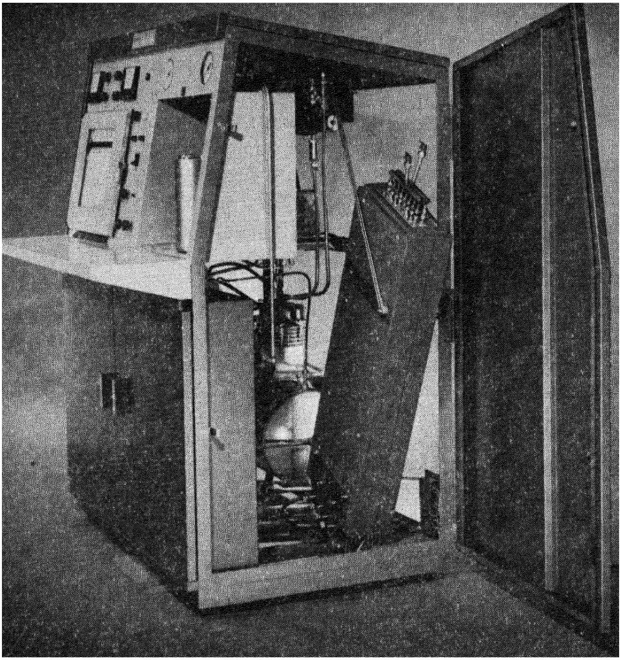

FIG. 2. Column and pump assembly.

minum plates. The aluminum block is heated by two flat sheath heaters one on each side of the block. Cooling coils are embedded in the aluminum plates for fast cooling or for operation of the columns at below ambient temperature.

Recycling of the carrier gas provides a considerable saving in operating cost, especially when one of the more expensive gases such as helium is used. Helium is normally recommended because it is inert toward the sample, is not inflammable, and has a liquefaction temperature considerably below the temperature of liquid nitrogen. Liquid nitrogen can then be used as a coolant for one or more of the clean-up traps shown in Fig. 3. The clean-up system consists of two large volume glass traps which may be cooled with any suitable coolant. Normally, water or ice water is used for the first trap and liquid nitrogen for the second trap. Residual sample material which may be so volatile that it is not completely removed by either of the two glass traps is taken out with a large volume adsorption trap which is located between the glass traps and the recycle pump. Figure 3 also shows three valves which make it possible to vent the entire carrier gas flow to the atmosphere, recycle the carrier gas, or reverse the action of the recycle pump in order to evacuate the ballast tank.

The purpose of the Megachrom preparative gas chromatograph, i.e., collection of purified fractions in practical amounts, requires a fraction collection system which is versatile and convenient to use. The fraction collection valve for this purpose is shown in Fig. 4. This valve has four collection traps connected by means of Swagelok fittings with Teflon ferrules for easy removal or replacement of traps without the use of wrenches. Traps may be of microtype for the collection of small samples which might require centrifuging to cause the collected fraction to accumulate in the cone shaped bottom of the trap or the traps may be of a macrotype for the collection of large samples. The traps are rotated in the coolant with the rotary collection valve which alternates the four trap positions with four bypass positions. The collection valve is motivated by a fractional horsepower motor through a Geneva drive mechanism which gives positive angular positioning as well as firm mechanical lock in all positions. The valve may be rotated in either direction and it is activated

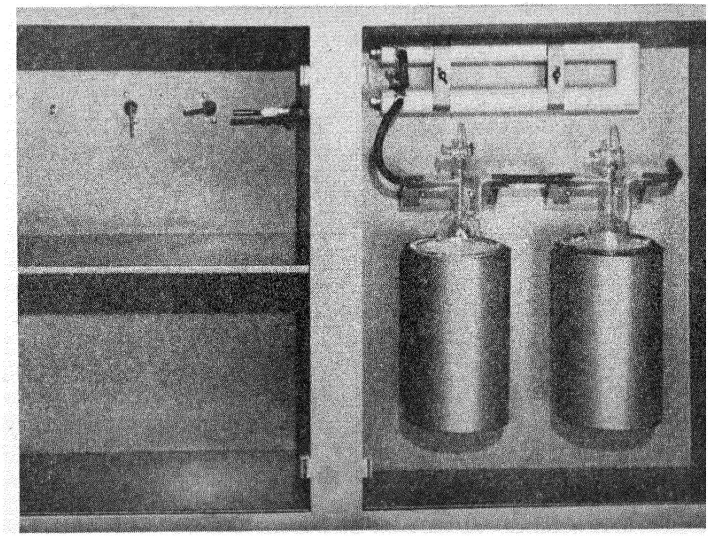

FIG. 3. Three-stage clean-up system.

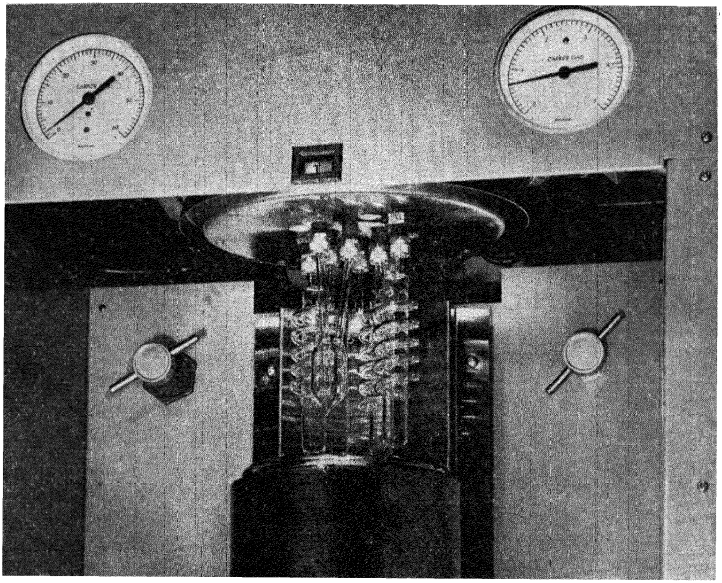

FIG. 4. Sample collection system.

manually with a push button control or automatically by means of a switch located in the recorder.

The fully transistorized, plug-in-type electronics in the instrument are shown in Fig. 5. Reading from top to bottom, the first plug-in chassis contains the power supply for the instrument and an on-off temperature controller for the sample inlet. The second chassis contains a magnetic amplifier which controls the column temperature. Full proportional control for column temperature is provided. Column temperature may be set to any temperature desired from ambient up to 315°C with the selector knob on the front panel and the trimmer pots shown in the upper right-hand corner of Fig. 5. Temperature of the column is read out on a meter mounted on the front panel. The third plug-in chassis contains a fully proportional controller for the detector temperature. It enables the operator to set the detector temperature to any of five preset temperatures up to 315°C. The fourth chassis is used for power distribution and contains a blower for cooling the electronics.

Figure 6 is a formal photograph of the Megachrom preparative gas hromatograph, showing the position of the various controls needed for he operation of the instrument.

APPLICATIONS

In order to check the performance of the instrument, three different pplications were selected which required wide variations in the operatng parameters.

The first application required the purification of commercial ethylbenene which was claimed to be approximately 99% pure. Identification of ome of the trace contaminants was also required. A chromatogram run vith 5.0 ml of the ethylbenzene is shown in Fig. 7. The major contamnants were benzene and heptane which were not separated by the paricular column used, Apiezon J. However, it was possible to identify both f the compounds from the infrared spectrum and elution time informa-

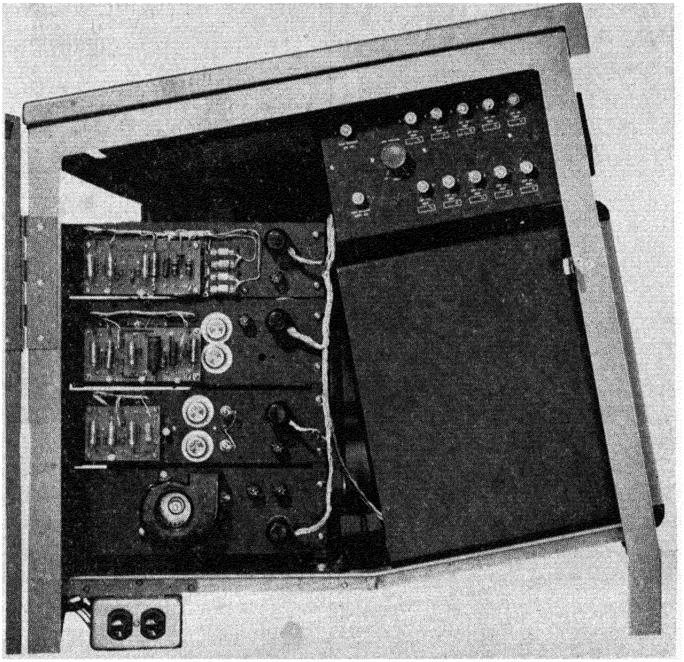

FIG. 5. Transistor electronics.

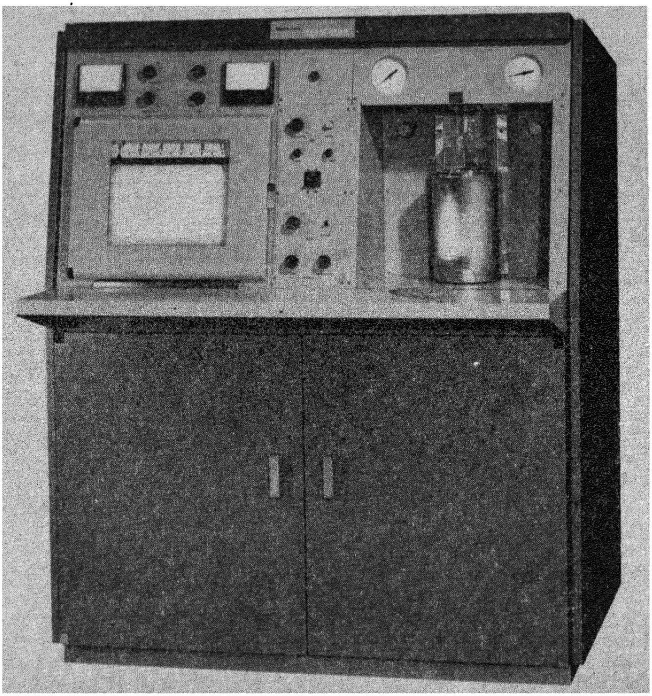

FIG. 6. Megachrom preparative gas chromatograph.

tion from the gas chromatograph. Infrared showed clearly that the collected fraction contained benzene and an unidentifiable straight-chain saturated hydrocarbon. Elution time information from the gas chromatograph indicated that the saturated hydrocarbon could only be heptane.

The other trace components were also identified by infrared. Some of the spectra are shown in Fig. 8. The superimposed spectra at the top of Fig. 8 were obtained with 99% ethylbenzene (lower curve) and the purified ethylbenzene (upper curve). Comparison of the spectrum for the original material with most reference spectra probably would not reveal the presence of impurities. However, the impurity bands become obvious when the curve is compared with that for the purified specimen.

The impurity band in the 2.9 μ region is accounted for by the presence of α-methylbenzyl alcohol. This compound also explains the increased ab-

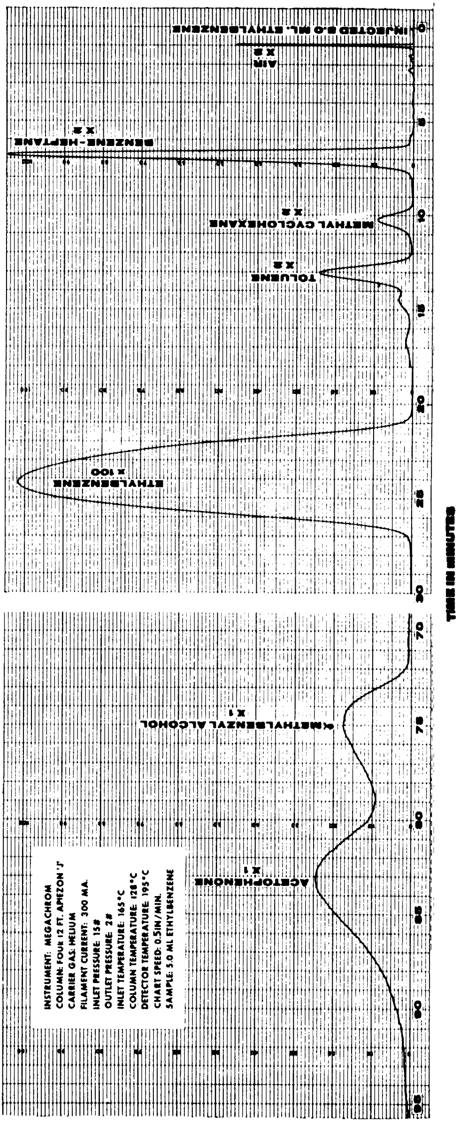

FIG. 7. Chromatogram of 5 0 ml of 99% ethylbenzene.

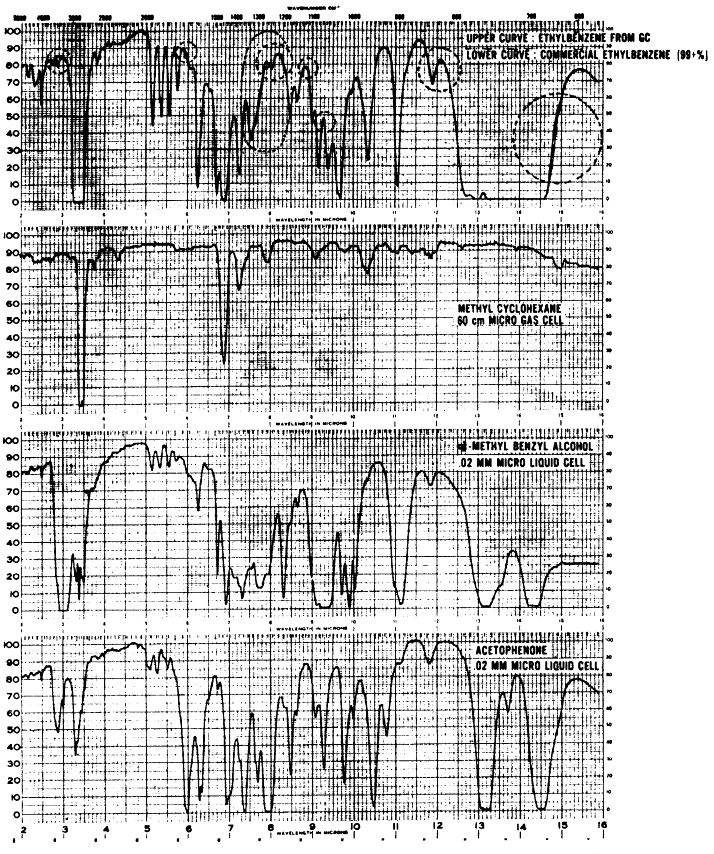

Fig. 8. Infrared spectra of ethylbenzene and fractions from ethylbenzene.

sorption of the 99% ethylbenzene in the 7.25 to 8.3 μ region. Increased absorption in the 9.3 μ region is explained by the presence of acetophenone. The increased absorption in the 14.7 to 15.0 μ region is probably due to contamination by benzene. The spectrum of acetophenone at the bottom of Fig. 8 shows more absorption in the 2.9 μ region than would be caused by the enol form of the ketone. This probably indicates slight contamination of this fraction with the α-methylbenzyl alcohol fraction.

Lemon oil was selected as the second sample for investigation. The first 40 minutes of a chromatogram obtained with 5.0 ml of this material is shown in Fig. 9. This application illustrates how identifiable fractions can be collected by taking a heart cut from unresolved components. It also demonstrates the feasibility of purifying minor components normally swamped by a preceding major component. Here, a time cut is obtained from successive samples such that the minor components are concentrated. The accumulated cut is then rechromatographed to isolate the minor components with acceptable purities.

Cut No. 1 has not been identified as yet but it is a terpene which does not show contamination from Cut No. 2 which was identified as a mixture of α-pinene and myrcene. Cut No. 3 was also collected without detectable contamination as shown by infrared. This fraction has been tentatively identified as β-phellandrene. The fourth cut was collected and identified as limonene, as shown by the spectrum at the top of Fig. 10. Cuts No. 5 and 6 were insufficiently resolved for the collection of identifiable fractions from the first run through the gas chromatograph. However, collection of the eluent over this portion of the chromatogram from three samples gave a sample which could be rechromatographed. This technique decreased the relative concentration of limonene so that Cuts No 5 and 6 could be collected essentially free from limonene. The spectrum of Cut No. 5 in Fig. 10 does not show significant contamination from limonene in the 12.5 and 13.2 μ regions which should be evident if limo-

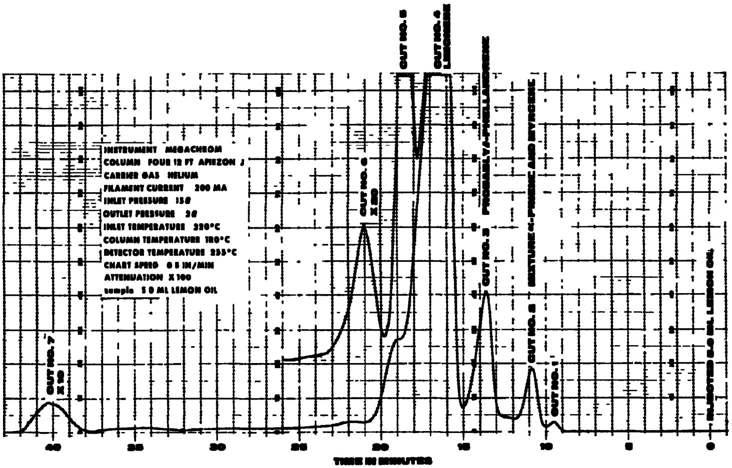

FIG 9 Chromatogram of 5 0 ml of lemon oil.

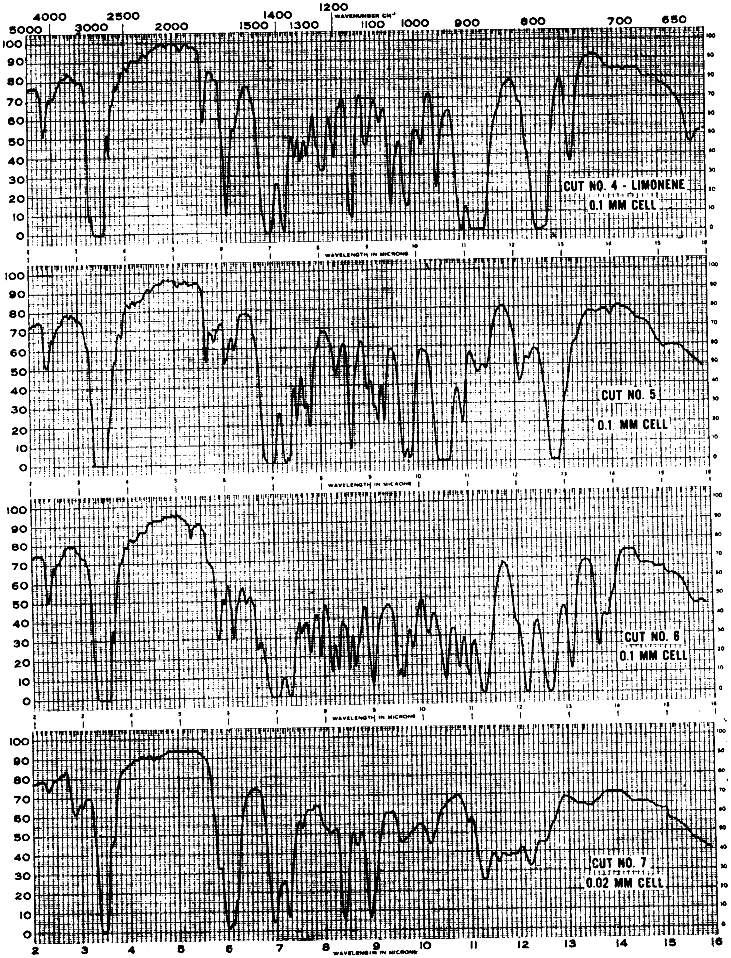

FIG 10. Infrared spectra of several fractions from lemon oil.

nene were present to an appreciable degree. The strong band at 12.8 μ in Cut No. 5 is missing from Cut No. 6, indicating that this fraction was also collected without significant contamination from neighboring components. Cut No. 7 was collected in a microtrap from the original 5.0 ml sample.

The third sample was selected to test the performance at high temperature of the inlet, the column, the detector, and the fraction collector valve. This sample contained a mixture of C_6 to C_{14} fatty acid esters, as shown in Fig. 11. Fractions were collected from methyl laurate and methyl myristate. These fractions were analyzed by infrared, as shown in Fig. 12. The two spectra at the top of this figure were recorded with the methyl esters from the gas chromatograph. The compounds could be identified as methyl esters with these two spectra, but positive identification as to a particular compound is impractical because of the minor differences between the two spectrograms. However, conversion of the collected fractions of methyl esters to the barium salts according to the method of Meiklejohn *et al.* (*9*) gave samples which could be positively identified by infrared, as shown in the spectra at the bottom of Fig. 12.

Column Performance

Although the chromatograms for the preceding applications appeared to be comparable to those previously obtained with conventional equipment using ¼-inch OD columns, it was considered desirable to check this point with a controlled experiment. The preparative gas chromatograph's column package, consisting of eight 6-ft, 0.625-inch ID columns arranged

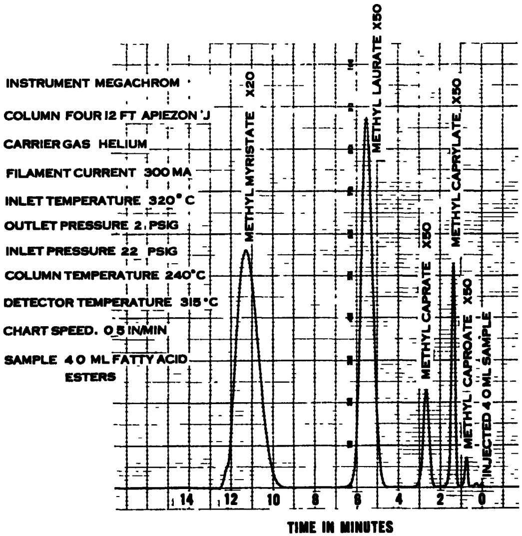

FIG. 11. Chromatogram of methyl esters of fatty acids from C_6 to C_{14}.

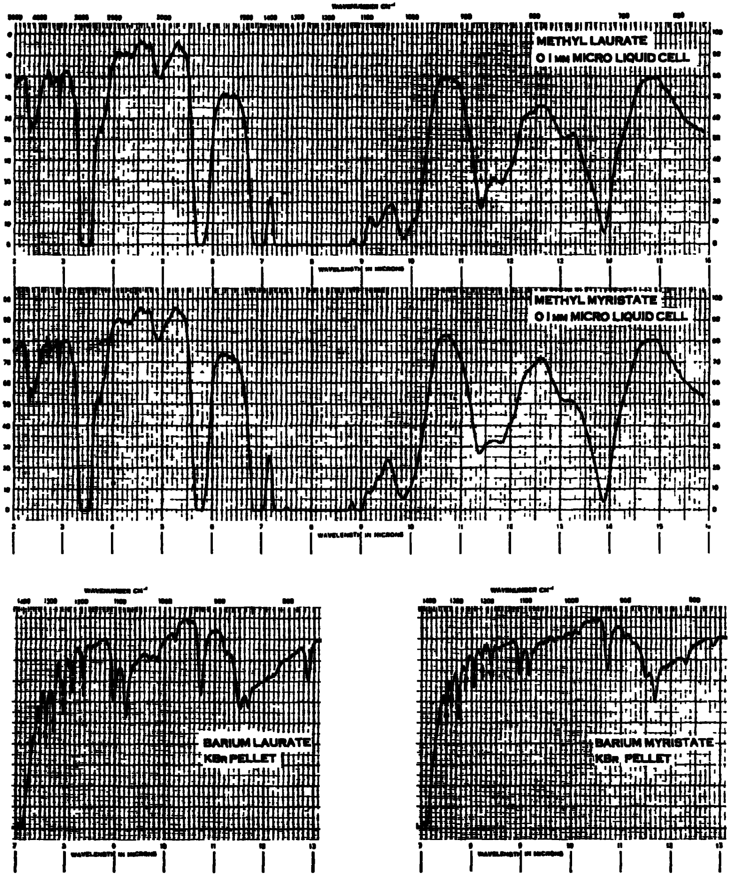

FIG. 12 Infrared spectra of gas chromatograph fractions of methyl esters and barium salts of fatty acids.

in parallel, was compared with a single 6-ft, 0.625-inch ID column. A 6-ft, 0.19-inch (¼ inch OD) column in a standard laboratory instrument was used as a standard for comparison.

All columns were packed with Apiezon J coated on 42–60 mesh firebrick at a concentration of 30% by weight. The temperature for all columns with both instruments was held constant at 128°C. The sample

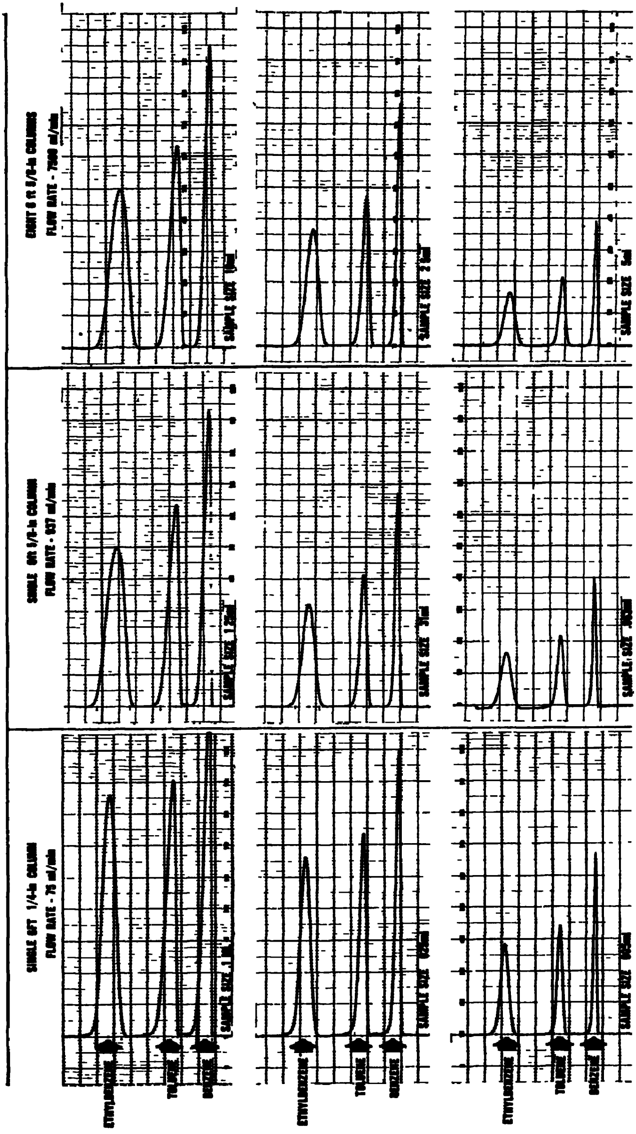

FIG. 13. Effect of column diameter and paralleling on performance.

mixture consisted of a solution of 30% benzene, 30% toluene, and 40% ethylbenzene in all cases. Helium was used as the carrier gas in all experiments. Both sample size and volume flow rate of carrier gas were scaled in proportion to the effective cross-sectional area of the columns. A comparison of the chromatographic records for the three column geometries employed is shown in Fig. 13. This figure shows that over the range of sample sizes tested that there was a slight but observable decrease in resolution when a ⅝-inch ID column is compared with a standard ¼-inch OD column. However, there did not appear to be any significant difference between a single ⅝-inch ID column and eight of these columns in parallel.

In order to obtain a more exact comparison, HETP (height equivalent to a theoretical plate) values were calculated for the toluene peak over a range of sample sizes for each of the three different column areas. A plot of this data is shown in Fig. 14. The HETP for a single ⅝-inch ID column increased slightly as expected when compared with a conventional ¼-inch column. However, the HETP value for eight ⅝-inch ID columns in parallel was slightly lower, especially at large samples sizes, than with a single ⅝-inch ID column. Since both of these sets of data were obtained with the same instrument the slight decrease in HETP with parallel columns cannot be explained on the basis of instrumental differences. The most logical explanation seems to be an improvement in sample flow to the column caused by the higher carrier gas pressure at the sample inlet needed to maintain the proportionate flow of carrier gas through the parallel columns.

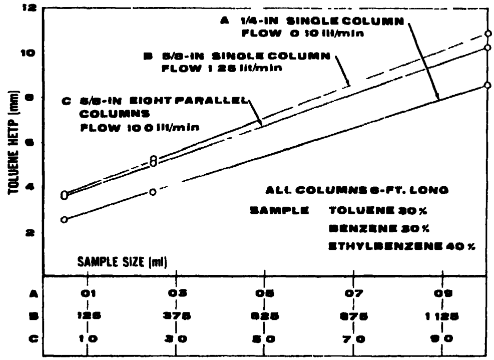

Fig. 14 Toluene HETP vs. column scale-up and sample size.

CONCLUSIONS

The highly efficient separatory power of gas chromatography can be retained with multigram samples by paralleling columns in order to increase the effective cross-sectional area. This greatly extends the usefulness of the gas chromatographic technique for the preparation of practical amounts of pure compounds and collection of trace contaminants for identification purposes.

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CHAPTER XXI

Quantitative Analysis of Complex Samples by Gas-Liquid Chromatography and Mass Spectrometry

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Gas-liquid chromatography frequently does not separate each and every compound present in complex mixtures. Although compounds that are not separated by one column packing often can be separated by another (*6*), there are many groups of compounds that are so similar in molecular structure and boiling point that complete resolution cannot be obtained even with multistage gas-liquid chromatography (*9*). Certain groups of isoalkanes present in petroleum alkylate samples, such as 2,3-dimethylbutane and 2-methylpentane-2,2-dimethylpentane and 2,4-dimethylpentane-2,3,3-trimethylpentane and 2,3-dimethylhexane, are particularly difficult to separate.

Under certain conditions, mass spectrometry has been combined with large-scale gas-liquid chromatography (GLC) to obtain more detailed semiquantitative analysis (*1*, *7*, *10*). However, Drew and McNesley (*3*, *4*) have indicated that special problems are encountered when fractions are collected from smaller scale gas-liquid chromatographic units for subsequent quantitative analysis by mass spectrometry.

The present report describes a suitable combination of a gas-liquid chromatographic technique with mass spectrometry which can be used to obtain both a quantitative "carbon number" distribution of full-range petroleum alkylate samples and a completely detailed quantitative analysis of all C_8 and lighter components. The results obtained are at least as reliable as those obtained by the combination of lengthy precision distillation with mass spectrometry, and the general technique should be applicable to other complex sample mixtures. An important problem, particularly with wide boiling-range samples, is the selection of a gas chromatographic column which will group compounds together that can be completely resolved by mass spectrometry and which will completely separate compounds that cannot be resolved.

"CARBON NUMBER" ANALYSIS

General Technique

An accurate appraisal of the composition of alkylate samples can be obtained with a highly efficient gas chromatographic column containing

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GE-96 (300) silicone fluid. This column liquid separates a wide variety of hydrocarbon types very nearly according to their boiling points. With isoalkane mixtures, this is approximately according to "carbon number." Using hot-wire thermal conductivity detection, very efficient boiling point separations are obtained with a ¼-inch by 15-ft column packed with GE-96 (300 viscosity) silicone fluid on 40–60 mesh aqua regia-treated C-22 firebrick (20gm/100gm). At 150°C and using a helium flow rate of 40 ml/min, this column has a separation efficiency of about 3000 theoretical plates, Full-range debutanized alkylate samples are separated at these conditions into C_4, C_5, C_6, two C_7, and three C_8 peaks, as well as several C_9, C_{10}, C_{11}, and higher peaks. All components in full-range alkylate samples emerge from the column held at 150°C in not more than 35 minutes. A typical chromatogram obtained at these conditions is shown in Fig. 1.

As will be seen later, almost every peak contains substantial amounts of other compounds of the same carbon number. Hence, when more than a carbon number distribution is required, the detailed composition of each peak must be determined.

Alkylate samples normally do not contain more than about 10%v of material boiling above 125°C. Therefore, in order to detect this material, a higher sensitivity must be used in this part of the chromatogram. The large number of C_9 and heavier isoalkanes makes it impractical at this time to obtain a positive identification of the components in the heavy end of alkylate. The GLC technique does, however, provide a rapid and reliable means of comparing the relative abundances of compounds of different boiling ranges. The retention times for n-C_9, n-C_{10}, and n-C_{11} are given on Fig. 1 to indicate the boiling ranges of the compounds represented by the several unidentified peaks. The other arbitrary boiling ranges indicated on Fig. 1 were established from retention time data for available isoalkanes.

Calibration Data

The peak area sensitivities of different hydrocarbons measured with a hot-wire thermal conductivity cell can vary over a wide range (*1*). Therefore, peak area calibration data are required before a quantitative interpretation can be made of the chromatogram given in Fig. 1.

Sensitivity data were determined for a large number of C_5–C_9 alkanes by charging different sample sizes of the pure compounds and measuring the peak areas thus produced with a planimeter. The peak area sensitivity is the peak area divided by the volume charged. It was found that the sensitivities decrease in the order of straight-chain alkanes > di-

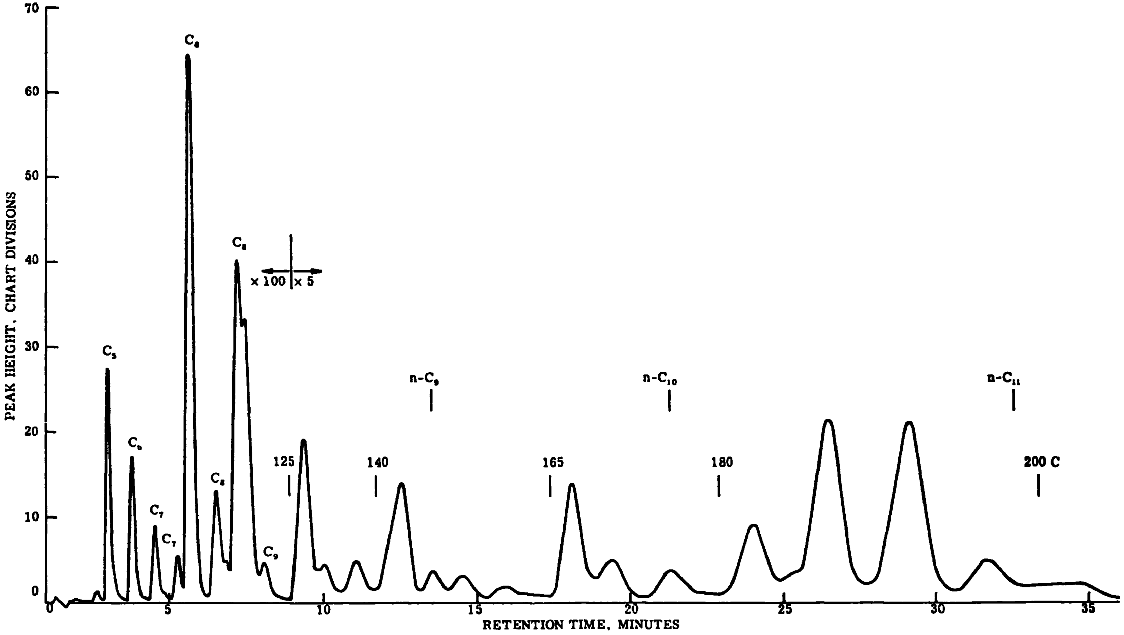

FIG. 1 Carbon number analysis of alkylate

GLC Conditions· Column, ¼-inch by 15-ft GE-96(300) silicone on 40–60 mesh aqua regia-treated firebrick (20 gm/100 gm); Temperature, 150°C; Helium flow rate, 40 ml/min; Sample size, 0 01 ml.

methylalkanes > trimethylalkanes > monomethylalkanes > tetramethylalkanes. The sensitivities of all alkanes of a given degree of branching are the same, and are independent of carbon number. Since the extent of branching in alkylate samples is in general also independent of carbon number, quantitative analyses can be obtained for alkylate samples directly from hydrocarbon peak areas. With other type samples, either the appropriate sensitivity data must be applied or a different type detector used.

Extensive calibration data are not required if the separated hydrocarbons are converted to CO_2 before detection by a modified CuO combustion procedure (*2*) similar to that described by Norem (*8*). Weight percentages can be obtained directly from the area of the CO_2 peak obtained (after removal of water with Dehydrite) by dividing this area by the percentage of carbon in the components represented. Although this procedure is not amenable to collecting hydrocarbon fractions for subsequent mass spectrometric analyses, it does provide a reliable method for quantitative interpretation of a gas chromatogram. Comparative data for alkylates have shown that compositions calculated from hydrocarbon peak areas are equivalent to those calculated from CO_2 peak areas.

COMPONENT ANALYSIS

GLC Separation

A pronounced separation of the C_8 and lighter components is desirable when cuts are to be taken for component analyses by the mass spectrometer. Consequently, once a carbon number distribution is obtained at a constant temperature of 150°C, the column temperature is reduced to 80°C. The heavy ends, of course, trail out of the column more slowly at this temperature. However, the C_8 and lighter components are recovered quantitatively and a chromatogram of the type shown in Fig. 2 is obtained. It has been found that improved resolution is achieved by treating the firebrick support with aqua regia prior to coating with silicone fluid (*11*). The aqua regia treatment markedly decreases band tailing although the number of theoretical plates is unaffected.

The entire chromatogram shown in Fig. 2 requires only 30 minutes of analytical time, although heavy ends continue to strip from the column for an additional 30 to 40 minutes. Cuts as indicated are collected in specially prepared traps cooled with liquid nitrogen, and each cut is analyzed by mass spectrometry for compounds that are likely to be present. In order to obtain reliable mass spectrometric analyses, the trapped cuts must be essentially free of contaminants from the following major sources: (a) water in the carrier gas, (b) atmospheric moisture, (c) entrainment

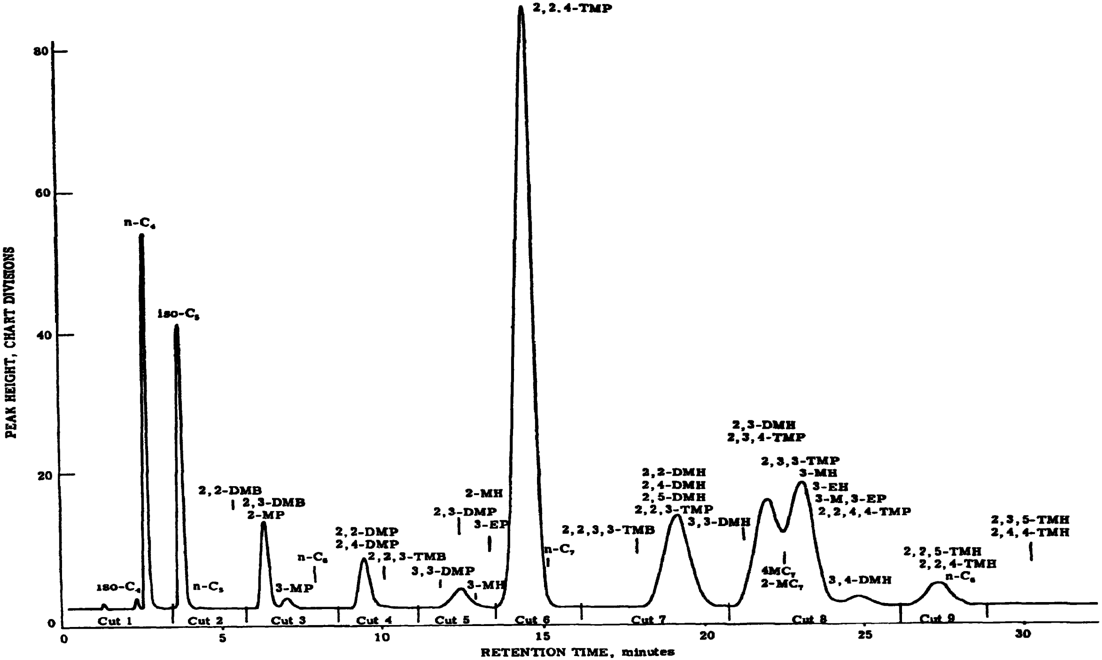

FIG 2 GLC separation for mass spectrometric analysis.

GLC Conditions: Column, ¼-inch by 15-ft GE-96 (300) silicone (20 gm/100 gm) on 40–60 mesh aqua regia-treated firebrick; Temperature, 80°C; Helium flow rate, 60 ml/min, Sample size, 0 01 ml; Peak components, as indicated.

of stationary liquid in the carrier gas, and (d) high-boiling components from a previous analysis.

Trapping Technique

The traps employed to collect cuts are shown in Fig. 3. High-vacuum, oblique-bore stopcocks are used on the inlet and exit lines of the traps. Three-way stopcocks are used on the inlet lines so that atmospheric (wet) air can be purged from the inlet line with effluent carrier gas from the GLC column just prior to collecting each cut. The fritted glass cylinder between the inlet and exit sides of the traps eliminate sample carryover losses due to "fog-type" entrainment.

Prior to an analysis the traps are cleaned with a suitable solvent; then they are heated several hours in a glass annealing oven at approximately 1200°F. The stopcocks are greased with Spectro-vac type II* stopcock grease, and the traps are evacuated to a pressure of 3 μ or less. While still connected to the vacuum system, each trap is immersed in liquid nitrogen just before use and filled with dry carrier gas to a pressure of 2–3 psig.

The traps are connected individually to the exit end of the GLC column by means of a short piece of Tygon tubing. The stopcock on the exit end is opened first to allow the excess carrier gas to escape. Then the three-way stopcock on the inlet is switched to allow the effluent from the GLC column to enter the trap. After the desired cut is taken, the inlet stopcock is switched to the bypass position and the exit stopcock is closed. Carrier gas is removed by reconnecting the traps to the vacuum system and pumping down to a pressure of about 10 μ. The traps then can be warmed to atmospheric temperature and submitted for mass spectrometric analysis.

Water can be removed from the carrier gas to mass spectrometric limits of detection by a ½-inch by 18-inch tube of Dehydrite placed in the inlet line to the GLC unit. High-boiling components remaining in the column from a previous analysis are eliminated by stripping the column for about one hour at 150°C during the "carbon number" analysis.

Analysis of Trapped Cuts

The specific mass spectrometric peaks used to prepare the matrix for each of the nine GLC cuts are tabulated in Table I. The mass spectrometric analysis of the lighter cuts, through cut 5, are straightforward and little or no difficulties are encountered. However, the heavier cuts become progressively more complex. The small unresolved peak at the end of cut

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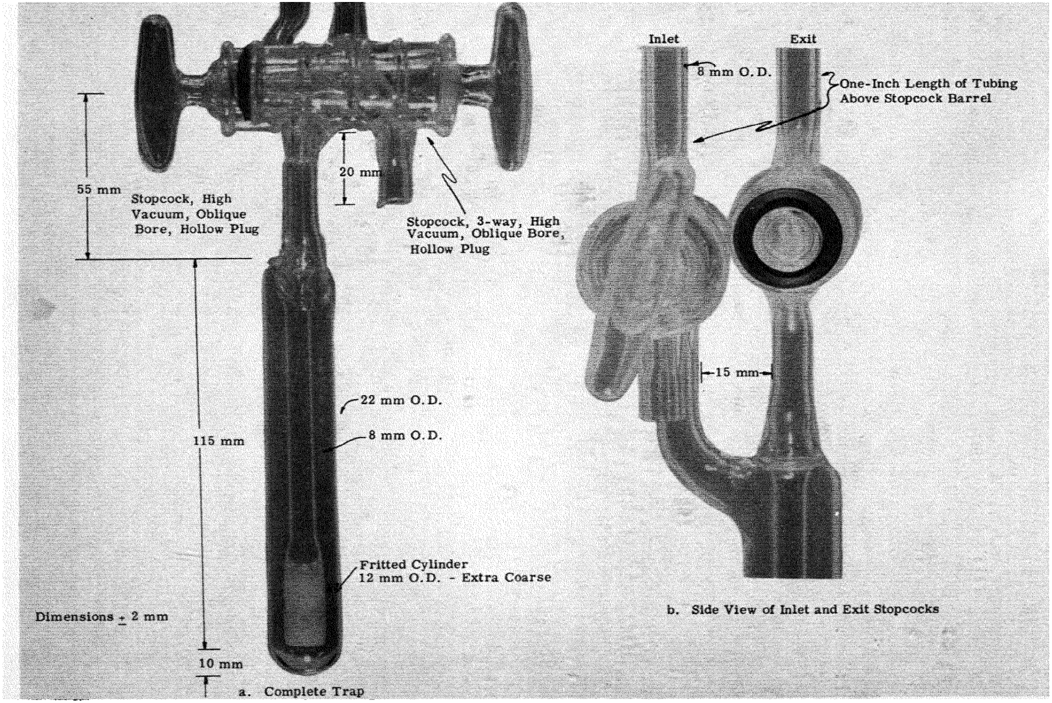
* Available from Robert R. Austin, Pasadena, California.



a. Complete Trap

b. Side View of Inlet and Exit Stopcocks

FIG. 3. Traps used to collect GLC cuts for mass spectrometric analysis. (a) Complete trap; (b) Side view of inlet and exit stopcocks.

TABLE I

MASSES APPLIED TO EACH GLC CUT IN COMBINATION GLC-MASS SPECTROMETRIC ANALYSIS OF ALKYLATES

Component	GLC cut number 1	2	3	4	5	6	7	8	9
Propane	29								
Isobutane	43								
n-Butane	58	58							
Isopentane	57	57							
n-Pentane	72	72	72						
2,2-Dimethylbutane		71	71						
2,3-Dimethylbutane		86	42						
2-Methylpentane		70	70						
3-Methylpentane			56						
n-Hexane			86						
2,2-Dimethylpentane			85	85					
2,4-Dimethylpentane			100	42	57				
2,2,3-Trimethylbutane				69	[a]				
3,3-Dimethylpentane				71	71				
2,3-Dimethylpentane				56	56	56			
2 Methylhexane					85	85			
3-Methylhexane					100	[a]			
3-Ethylpentane					70	70			
2,2,4-Trimethylpentane						57			
n-Heptane						100			
2,2,3,3-Tetramethylbutane						[a]	[a]		
2,2-Dimethylhexane						[b]	57		
2,4-Dimethylhexane						[a]	85		
2,5-Dimethylhexane						112	112	[a]	
2,2,3-Trimethylpentane							56	57	
3,3-Dimethylhexane							[a]	[a]	
2,3,4-Trimethylpentane							71	71	
2,3-Dimethylhexane							70	70	
4-Methylheptane								[a]	
2-Methylheptane								114	
2,3,3-Trimethylpentane								(55+69+85+99)	
3,4-Dimethylhexane								56	
3-Methylheptane								84	
2,2,5-Trimethylhexane									[c]

NOTE Components are listed in order of GLC emergence

[a] Not included, qualitatively indicated to be absent

[b] Mass spectrometer cannot resolve 2,2,4-trimethylpentane and 2,2-dimethylhexane in the same cut, however, because of the boiling point separation accomplished by GLC, 2,2,4-trimethylpentane is present in cut 6 only, and 2,2-dimethylhexane is present in cut 7 only

[c] Major component Direct comparison with pure compound spectrum indicates 99+% 2,2,5-trimethylhexane

8 was found to be 3,4-dimethylhexane by collecting it separately for mass spectrometric analysis. On the other hand, cut 9 was found to be 99+ % 2,2,5-trimethylhexane.

The mass spectrometric (MS) analyses of cuts collected from the alkylate separation shown in Fig. 2 are given in Table II. The amount of total alkylate in each cut is determined by the more rapidly obtained "carbon number" analysis. The amount of each component then is obtained by normalizing the composition of each cut to the amount of total alkylate in each cut, and combining values when a component is contained in more than one cut.

Comparative component analyses obtained in this manner by the GLC-MS technique are given in Table III for finished alkylate samples produced by H_2SO_4 and by HF catalysts. These analyses reflect differences in butylene feed composition and operating conditions as well as changes caused by the acid catalyst used. Moreover, the results are consistent with those reported by Glasgow *et al.* (*5*) for 15 samples of H_2SO_4 alkylate and 5 samples of HF alkylate. Their analyses were obtained by lengthy precision distillations lasting 1000 hours or more, and 250 or more cuts were analyzed from each distillation. The material boiling above 124°C could be identified by boiling range only. The present GLC-MS technique accounts for 90% or more of the compounds present in finished alkylate, and it provides a more detailed breakdown of the dimethylhexanes than was reported by Glasgow *et al.* For example, 2,4- and 2,5-dimethylhexane are determined separately and it is possible to observe that the HF alkylate contains more 2,4-dimethylhexane than 2,5-dimethylhexane, whereas this concentration ratio is reversed in the H_2SO_4 alkylate.

The component analysis provides considerably more detail than the carbon number analysis. For example, while cut 3 is predominantly 2,3-dimethylbutane, appreciable quantities of 2- and 3-methylpentane are detected. In addition, the component analysis accurately determines the ratio of 2,2,3-trimethylpentane to 2,4- and 2,5-dimethylhexanes in cut 7, and the amounts of 2,3-, 3,3-, and 3,4-dimethylhexanes that are present in cut 8, as well as the exact amount of 2,3,4- and 2,3,3-trimethylpentane. An interesting supplement to the component analyses is the list of compounds that were looked for but found not present. For example, although both alkylates contained appreciable quantities of 2,2,3-trimethylpentane, neither contained more than trace amounts (<0.04 %v) of: 2,2-dimethylbutane, 2,2,3-trimethylbutane, 3,3-dimethylpentane, 3-ethylpentane, 2,2-dimethylhexane, 4-methylheptane, or 2-methylheptane. Of course, neither contained normal paraffins such as *n*-hexane, *n*-heptane, or *n*-octane.

TABLE II
COMPONENT ANALYSIS OF ALKYLATES: MASS SPECTROMETRIC ANALYSIS OF GLC CUTS

Component	GLC Cut Number								
	1	2	3	4	5	6	7	8	9
Propane	—								
Isobutane	2.6								
n-Butane	97.4	—							
Isopentane	—	100.00							
n-Pentane	—	—	0.3						
2,2-Dimethylbutane		—	—						
2,3-Dimethylbutane		—	64.3						
2-Methylpentane			24.7						
3-Methylpentane			10.7						
n-Hexane			—						
2,2-Dimethylpentane			—	7.9					
2,4-Dimethylpentane			—	87.8	0.1				
2,2,3-Trimethylbutane				—	—				
3,3-Dimethylpentane				—	—				
2,3-Dimethylpentane				4.3	76.4	—			
2-Methylhexane					15.0	—			
3-Methylhexane					7.8	—			
3-Ethylpentane					0.7	—			
2,2,4-Trimethylpentane						99.8			
n-Heptane						—			
2,2,3,3-Tetramethylbutane						—	—		
2,2-Dimethylhexane						—	—		
2,4-Dimethylhexane						—	46.5		
2,5-Dimethylhexane						0.2	38.8		
2,2,3-Trimethylpentane							14.0	0.4	
3,3-Dimethylhexane							—	—	
2,3,4-Trimethylpentane							—	40.8	
2,3-Dimethylhexane							0.7	20.5	
4-Methylheptane								—	
2-Methylheptane								0.4	
2,3,3-Trimethylpentane								34.5	
3,4-Dimethylhexane								2.5	
3-Methylheptane								0.8	
2,2,5-Trimethylhexane									99+
Sum, basis cut	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sum, basis total alkylate	5.0	5.1	3.7	2.2	1.6	38.1	9.0	23.6	3.2

TABLE III

GLC-MASS SPECTROMETRIC COMPONENT ANALYSES OF FINISHED ALKYLATES

Component	H_2SO_4 alkylate, % v[a]	HF alkylate, % v[a]
Propane	0.05	—
Isobutane	0.04	0.13
n-Butane	0.92	4.87
Isopentane	8.76	5.10
n-Pentane	0.23	0.01
2,2-Dimethylbutane	—	—
2,3-Dimethylbutane	5.36	2.38
2-Methylpentane	1.29	0.91
3-Methylpentane	0.64	0.40
n-Hexane	—	—
2,2-Dimethylpentane	0.25	0.17
2,4-Dimethylpentane	3.62	1.95
2,2,3-Trimethylbutane	0.01	—
3,3-Dimethylpentane	0.01	—
2,3-Dimethylpentane	2.15	1.31
2-Methylhexane	0.22	0.24
3-Methylhexane	0.14	0.12
3-Ethylpentane	0.01	0.01
2,2,4-Trimethylpentane	24.20	38.02
n-Heptane	—	—
2,2,3,3-Tetramethylbutane	[b]	[b]
2,2-Dimethylhexane	0.04	—
2,4-Dimethylhexane	2.89	4.19
2,5-Dimethylhexane	4.94	3.57
2,2,3-Trimethylpentane	1.53	1.35
3,3-Dimethylhexane	[b]	[b]
2,3,4-Trimethylpentane	13.15	9.63
2,3-Dimethylhexane	3.41	4.90
4-Methylheptane	—	—
2-Methylheptane	0.08	0.09
2,3,3-Trimethylpentane	11.47	8.14
3,4-Dimethylhexane	0.26	0.59
3,Methylheptane	0.23	0.19
2,2,5-Trimethylhexane	7.20	3.20
	93.10	91.50

[a] Basis total finished alkylate.

[b] Qualitatively indicated to be absent.

The GLC-MS technique has been applied to light straight-run gasolines and catalytic reformates. Here again the choice of column packing and cut points must be determined by the groups of compounds which can be handled, without mutual interference, by the mass spectrometer.

SUMMARY

Under certain conditions, mass spectrometry can be combined with gas-liquid chromatography to obtain a more detailed analysis than can be obtained by either method alone. Quantitative component analyses of complex sample mixtures often are possible when a gas chromatographic system can be selected which is compatible with the requirements of mass spectrometry both with regard to the types of compounds that are grouped together and the extent to which objectionable contaminants are eliminated. A method employing these principles has been successfully applied to the complex mixture of paraffinic hydrocarbons found in petroleum alkylate.

ACKNOWLEDGMENT

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CHAPTER XXII

Confirmatory Tests in Gas Chromatography

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One of the recurring analytical problems in our laboratory is the analysis of solvents, such as dry-cleaning fluids, paint thinners, floor cleaners, degreasing solvents, etc. It is desirable to be able to determine whether a given solvent contains aromatic or chlorinated hydrocarbons, since these are toxic. It is desirable also to be able to tell which aromatic or chlorinated hydrocarbon is present. In such analyses, gas chromatography has has proved of great value. It is very easy, for example, to establish the number of compounds present, and their proportions. It is not, however, easy to decide what a particular peak on a recorder chart represents. For instance, one cannot say that a particular peak represents one of the chlorinated hydrocarbon class; still less, which specific chlorinated hydrocarbon.

Other workers in gas chromatography have identified particular components by their retention times or retention volumes (*1*). This procedure is, of course, satisfactory where one is working with a simple mixture whose composition is already known or when working with a mixture of homologs, whose properties, to some extent, are predictable on the basis of their position in the series. James determined 6 pyridine homologs and 27 aliphatic amines by their retention volumes.

As the solvents and solvent mixtures we encounter may be from different sources, different manufacturers, may be destined for different end uses, and may vary in composition for economic reasons, the analyst's task is formidable. It is not made easier by the fact that the composition is not usually given on the label. On the contrary, the identity of the material may be hedged in secrecy under some proprietary name. The unit solvents from which such mixtures are made are not likely to be of reagent grade, but will be of commercial quality, probably themselves consisting of more than one component. The final made-up solvent mixture, as sold, can contain five to twenty compounds in varying proportions. These components may include such varied materials as esters, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, ethers, alcohols, and chlorinated hydrocarbons.

There would seem to be an obvious need for simple confirmatory tests which could identify a peak while the chromatogram is in progress, at least within broad chemical classes. In our work, for example, even the availability of such definitive tests for chlorinated hydrocarbons and aromatics would simplify our analyses greatly. The presence of esters, ketones, aliphatics, and others are usually of secondary interest to us. Berridge and Watts have made quantitative measurements on six ketones on the effluent from the column. The ketone in vapor form was reacted with hydroxylamine hydrochloride, which liberated free acid, and the change in pH was measured semicontinuously (*2*). James and Martin determined eight fatty acids from acetic to *n*-valeric by gas chromatography followed by continuous titration of the effluent from the column (*3*) Liberti determined eight fatty acids in the effluent gas by manual coulometric titration. He also analyzed a synthetic mixture of five mercaptans by coulometric analysis of the effluent (*4*).

These workers have developed quantitative chemical tests as cited. The downstream responses are measured in terms of changes of alkalinity, acidity, pH, transmittance, etc., which are not specific responses. It is a prerequisite that the analyst work with members of one chemical class at a time, which will separate successfully under the conditions used, and which will give a quantitative response to the particular downstream sensing system. Substances which do not respond quantitatively, must be absent from the sample under test. The analyst must really know the composition of his sample before he can make use of his downstream tests.

Since the tests mentioned above are not qualitative, we considered that, for our purposes, specific confirmatory tests would be more useful. For some time, therefore, we have been working on the problem of such test development. Previously, we had reported a test for ketones which was specific and sensitive (*5*). The success of this test helped orient us in the present investigation. At the outset of this investigation, therefore, we decided, partly on the basis of past experience, that suitable tests should meet the following specifications:

(1) The confirmatory tests must be sufficiently rapid to be essentially coincident with peak appearance.

(2) The test must be simple and applicable to the isolated gaseous component in the column effluent.

(3) The test must be sensitive to one microliter or less of the pure isolated component.

(4) It should be specific for chemical groups, but not necessarily specific for individual members of the group.

(5) It must be readily adaptable to automatic analysis and sample collection, without requiring the operator's attention.

(6) It must be simple enough for untrained operators to obtain reliable results.

(7) It should not involve expensive ancillary instrumentation, since the average laboratory would have difficulty justifying such additional expense.

(8) If possible, the test should be destructive only of the individual components of the group being tested for, so that several chemical classes might be identified simultaneously by a series test train.

Before choosing the working specifications cited, we had carried out some investigation of infrared (IR) identification of individual components trapped in carbon tetrachloride. In our admittedly small experience, these were limited in utility, since to achieve sensitivity with the infrared instrument it was necessary to load the column heavily. The IR identification, of necessity, cannot be simultaneous but requires a minimum of fifteen minutes time lag behind the corresponding component peak. Some infrared patterns of components separated from the commercial solvents by gas chromatography are shown in Fig. 1. Not having much experience

FIG. 1. Infrared patterns of components separated from commercial solvents by gas chromatography.

with infrared interpretation we found it difficult to identify the components from these curves. The possibility of simultaneous infrared identification, using special flow-through cells, was not considered because of item 7. We concluded that since the feature of rapid identification was essential, that infrared analysis would not be too useful to us.

In our work we chose the path of least resistance, investigating first the materials for which on *a priori* grounds we expected suitable tests could be rapidly developed. We have already mentioned such a test for ketones (*5*).

PRELIMINARY SAMPLE TREATMENT

Certain simple chemical tests should always be applied to the original material before gas chromatography. If dissolved or suspended solids are present, it is necessary to remove these to avoid fouling the detector. Preliminary evaporation, filtration, or distillation may be advantageous. The degree of solubility in water should be established. If a two-phase system results, with the organic phase underneath, this will probably indicate the presence of halogenated hydrocarbons. Even better, a Beilstein test, which will establish quite definitely the presence or absence of halogenated hydrocarbons, should be carried out on the original material. The analyst should note the original color and odor of the material. Using only an experienced nose, it is relatively easy to determine the presence of one or more of the following classes in mixtures: ketones, esters, chlorinated hydrocarbons, and aromatic hydrocarbons.

APPARATUS

We used in this work a Perkin-Elmer Fractometer Model A. This we modified to shorten the length of tubing from the exit end of the detector to the practical minimum. This was to reduce, as much as possible, the time lag between peak appearance and the arrival of a component in the sampling receiver. Usually, 6-inch hypodermic needles, 22-gage, were attached to the effluent tubing exit and used to introduce the component being separated into simple receivers, such as 15-ml centrifuge tubes, or homemade capillary borosilicate glass tubes. Samples were introduced to the column by injection with an Agla microsyringe.

KETONES

Reagents and Procedure

In this test, the effluent gas from the column is passed through the 6-inch hypodermic needle which dips into 0.5 to 1.0 ml of 2,4-dinitrophenylhydrazine solution contained in a 15-ml centrifuge tube. For micro-

TABLE I

KETONE DETECTION TESTS

Ketone	Limit of detection, µl	Color of precipitate
Acetone	0.1	Yellow
Methyl ethyl ketone	0.1	Yellow
Methyl isopropyl ketone	0.1	Yellow
Methyl isobutyl ketone	0.2	Yellow
n-Butyl ethyl ketone	0.2	Yellow
Cyclohexanone	0.4	Yellow
Mesityl oxide	0.5	Red

liter amounts of ketones a positive test is obtained. As the ketone component bubbles through the clear reagent the solution becomes slightly turbid and opalescent. With longer bubbling (1–2 min) a yellow to orange precipitate of the 2,4-dinitrophenylhydrazone is formed by aggregation. Ketones which have been tested in this procedure, with limits identifiable, are shown in Table I.

Positive tests were obtained for microliter amounts of each of the pure ketones, injected on the column, and tested on the effluent. The above limits of detection were established by injecting dilutions of the ketones in ethanol, which made it easier to measure and inject such small quantities of material.

Interferences

As is well known, ketones and aldehydes both give a positive test with 2,4-dinitrophenylhydrazine. In actual practice, aldehydes, with the exception of furfural, are unlikely to be present in solvents. Ethanol, benzene, toluene, methyl chloroform, ethyl acetate, isopropyl acetate, and acetic acid gave no response with this test in 10 µl amounts. Methyl acetate gave a positive test. This proved to be due to the presence of a ketone impurity in the reference sample of methyl acetate which had been used (E.K. No. 520). The ketone test described meets requirement 1. The sensitivity (requirement 3) could perhaps be improved by determining the optimun conditions for insolubility of the phenylhydrazone.

ESTERS

For the identification of esters the well-known hydroxamic color test was adopted (*6*).

Reagents

Sodium Hydroxide: 12.5% in methanol.

Hydroxylamine Hydrochloride: 12.5% in methanol.

Ferric Perchlorate Stock Solution: Dissolve 5.0 grams of ferric perchlorat in 10 ml of 70% perchloric acid and 10 ml of water. Dilute to 100 n with anhydrous ethanol, cooling in cold water as the alcohol is addec This stock solution is stable for more than one month when stored i the refrigerator.

Reagent Solution: To 40 ml of the stock solution, 12 ml of 70% pe chloric acid is added, which is then diluted to 1 liter with anhydrou ethanol. The dilution should be carried out by adding alcohol in 50–10 ml portions, cooling under cold running water between each additio

Procedure

The effluent gas from the Fractometer is bubbled into an alkaline sol tion of hydroxylamine hydrochloride. This solution is prepared, just befor use, by mixing equal volumes (4 drops) of sodium hydroxide and hy droxylamine hydrochloride. Ten minutes after the sample has been co lected the ferric perchlorate reagent is added drop by drop until the fe ric hydroxide is completely dissolved (pH 2). At this point a violet colo indicates a positive test for esters. Samples of relatively pure esters (East man reagent grade) were injected and tested at the effluent end. Tabl II lists esters which gave a positive test in the procedure described.

It may be noted from the column headed "Impurities" that the "pure esters usually contained more than one component, as determined by th

TABLE II

Esters Giving Positive Test

Ester	Impurities	Limit of detection, μl	Retention time, sec
Methyl acetate	2	0.04	213
Ethyl formate	4	0.04	213
Ethyl acetate	2	0.04	292
Isopropyl acetate	2	0.06	349
Ethyl propionate	4	0.04	427
n-Propyl acetate	5	0.06	517
sec-Butyl acetate	3	0.06	629
Isobutyl acetate	2	0.05	696
Ethyl *n*-butyrate	—	0.06	775
n-Butyl acetate	3	0.06	978
n-Butyl acetate	3	0.06	978
Isoamyl acetate	3	0.07	1340
n-Amyl acetate	3	0.07	1830
n-Hexyl acetate	2	0.09	3560
n-Heptyl acetate	—	0.10	6650
Phenyl acetate	1	0.10	8340

gas chromatogram. Ester tests were directed at the effluent corresponding to the main peak. Five microliter quantities of the "pure" ester all gave positive tests. To determine the limit of detection more exactly as shown in Table II dilutions of the ester in alcohol were injected and tested.

Interferences

Ethanol, acetone, toluene, acetic acid, benzene, methyl chloroform, carbon tetrachloride, and monochlorbenzene gave no response with the test. According to Cheronis and Entrikin, a positive test may be given in this reaction by anhydrides, acid chlorides, and formic acid. We have confirmed that formic acid gives a positive test. Anhydrides and acid chlorides are not likely to occur in solvent mixtures. The column used during this work was a Perkin-Elmer A which uses a phthalate ester as the stationary liquid. In connection with this ester test it must be admitted that it does not meet requirement 1. It is thought worthy of consideration, however, due to its sensitivity.

AROMATIC HYDROCARBONS

Reagents and Procedure

The reagent solution is prepared by mixing 1 ml of concentrated sulfuric acid with 2 drops of 37% formaldehyde solution. This is made up just prior to use. The effluent gas from the column is bubbled into this solution. Table III lists aromatic hydrocarbons which gave positive tests.

Interferences

All samples were diluted in ethyl alcohol before injection. The following materials, including ethyl alcohol, gave no response in the test: ethyl alcohol, methylene chloride, methyl chloroform, isopropyl acetate, methyl acetate, and acetone. Phenyl acetate gave a positive test due to the presence of the benzene nucleus.

TABLE III

HYDROCARBONS GIVING POSITIVE TEST

Hydrocarbon	Limit, μl	Color
Benzene	0.5	Cherry red
Toluene	0.5	Cherry red
o-Xylene	0.6	Cherry red
m-Xylene	0 6	Cherry red
p-Xylene	0.6	Cherry red

ALIPHATIC ALCOHOLS

Reagents and Procedure

Ten grams of ammonium hexanitratocerate (ceric ammonium nitrate) is dissolved in water and made up to 100 ml. The effluent gas from the column is bubbled into a few drops of the reagent solution contained in a 15-ml centrifuge tube. Table IV lists alcohols which gave positive tests.

Interferences

All samples were diluted in acetone before injection. The following materials, including acetone, gave no response in the test: acetone, benzene, methyl chloroform, methyl acetate, tetrachloroethylene, and commercial xylene.

HALOGENATED HYDROCARBONS

Excellent group specificity and sensitivity was obtained by using a modified Beilstein test. Column effluent containing chlorinated hydrocarbons was directed through the exit hypodermic needle into a simple gas burner, as illustrated in Fig. 2. This burner has a metal base, the rest is glass. A plug of glass wool is inserted to disperse the gas stream, and a copper wire helix of suitable size is positioned in the flame. The burner is fed with natural gas at 6 inches water pressure, and the flame is adjusted for minimum luminosity and maximum stability. When chlorinated hydrocarbons are present a green color is imparted to the flame. Table V lists chlorinated hydrocarbons with detectable limits which were tested in this way.

With regard to identification limits it is realized that the test is somewhat subjective. It also depends on the visual acuity and accuracy of color vision of the operator.

TABLE IV

ALCOHOLS GIVING POSITIVE TEST

Alcohol	Limit, μl	Color
Methyl	0.4	Amber
Ethyl	0.4	Amber
Isopropyl	0.5	Amber
n-Propyl	0.5	Amber
n-Butyl	0 8	Amber

NOTE: With higher concentrations of alcoholic hydroxyl group a red color rather than amber may be obtained

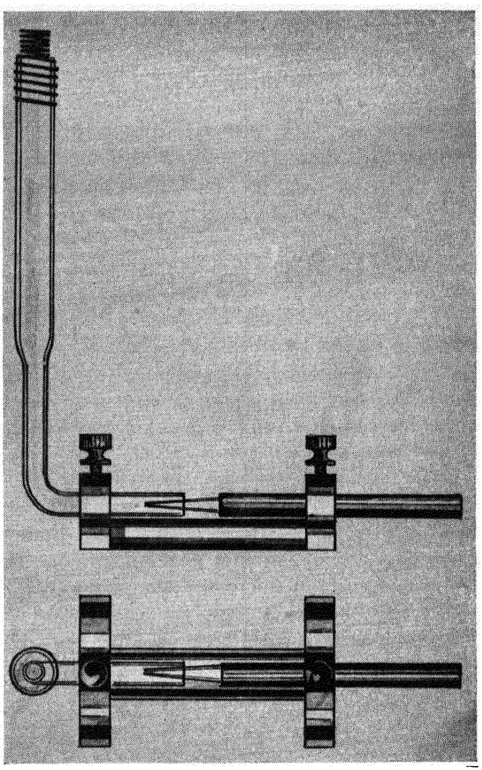

Fig. 2. Apparatus for detecting halogenated hydrocarbons by means of modified Beilstein test.

TABLE V

Halogenated Hydrocarbon Detection Test

Halogenated hydrocarbon	Limit, μl
Carbon tetrachloride	0.13
Chloroform	0.2
Methyl chloroform	0.2
Methylene chloride	0.4
Trichlorethylene	0.7
Ethylidene chloride	0.2
Ethyl bromide	0.2

Elaborating on this test further we have developed it, with suitable instrumentation, to the point where an automatic visual recording of the Beilstein reaction can be made on the effluent from the gas chromatographic column. Since a photocell response is used this allows one to use a color-blind operator. This serves the purposes of confirming the presence of chlorinated hydrocarbons without need for operator attention and a permanent record of a positive test is made which can be used for a quantitative and qualitative measure of halogen content of the original halogenated compound. This procedure is to be reported in a separate paper.

Interferences

A positive response to the Beilstein test is given by brominated and iodinated compounds as well as by chlorinated hydrocarbons. Compounds in which fluorine is the sole halogen give no response. Again, in solvent analysis, for most practical purposes the reaction may be considered specific for chlorinated hydrocarbons.

SUMMARY

A systematic identification procedure is described suitable for use in solvent analysis by gas chromatography. Positive tests are obtained with the compounds investigated at essentially the same time as the peak occurs on the chromatogram. It is hoped to extend this work to other classes of organic compounds. Work is proceeding with chemical confirmatory tests in series arrangement which is being reported separately. It is hoped the above procedure will stimulate other workers along these lines.

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CHAPTER XXIII

The Development of an Idea

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I should like to thank the Instrument Society of America, Mr. Brenner, Mr. Noebels, and Mr. Coates for their kind invitation to address this conference. As I have gathered that a purely technical paper might tire the audience, I have chosen to speak on the historical development of the gas-liquid chromatogram. This, I hope, when taken together with Dr. A. J. P. Martin's speech at your last meeting, will give our combined views.

My link with Dr. A. J. P. Martin was formed initially by chromatography. My introduction to this subject was brought about by working with Dr. R. L. M. Synge at the Lister Institute on the structure of an antibiotic polypeptide—Gramicidin. After Synge had left the Lister Institute to go to the Rowett Research Institute, Martin joined the Medical Research Council Staff and worked at the Lister Institute until the new laboratories at Mill Hill were ready.

At the time, I was separating derivatives of the amino sugars on a liquid-liquid chromatogram and required a fraction collector. Martin and I worked together on the design of a simple siphon operated mechanical device, and in this way I had my first experience of Martin's phenomenal experimental ability. He belongs to the great string and sealing wax school; in fact, with these materials and a little glass blowing he can accomplish more than most people can do with the most complex electronic and mechanical apparatus.

As you heard from Martin at the last Instrument Society Meeting, we first worked together on fractional crystallization—in fact we were trying to invent zone melting but did not succeed. We were using a 4 ft length of 4-mm I.D. glass tubing packed with Celite through which solvent was passed. A copper tube, hot at one end and cold at the other, was moved slowly along the tube after the crystalline mixture was added in solution.

I was rather despondent at my failure to get much of a separation and possibly the sight of the long packed column reminded Martin of his earlier suggestion of the gas-liquid chromatogram. Largely in order to cheer me up, he suggested that we try this as our next problem.

We used 4-mm I.D. glass columns packed with ungraded Celite 545 wetted with liquid paraffin and tried to separate the short chain fatty acids.

As a detector we used a test tube filled with aqueous indicator that we titrated dropwise, timing the drops with a stopwatch. Our separations were poor, the bands tailed badly and overlapped. We thought that adsorption was the complicating factor and tried a variety of supports for the stationary phase; sand, powdered Carborundum, salts, and even a capillary column with no packing, but still the bands were distorted. For many weeks we could not understand why we were getting such behavior.

Finally, almost in desperation, we decided to try compounds other than fatty acids. Our choice was the methylamines—(a) because they could be titrated in an aqueous medium and (b) because they had some biochemical interest.

Our very first try with these substances was successful—we got clear separations. Having proved our point—the feasibility of the gas-liquid chromatogram—we now had to decide why it did not work with the fatty acids.

During this time I had been learning Martin's famous precepts of research:

1. Never do the first experiment too carefully, i.e., the minimum of instrumentation.
2. Never do too many experiments.
3. Nothing is too much trouble provided someone else does the work.

Martin would never do any experiment without the most careful and protracted thought, time for consideration often extending to many weeks. This had the result that he was usually able to discard 99 experiments and do only the critical 100th experiment that would give a definitive answer to the question. Over a few weeks thought, the answer to the fatty acid problem emerged: in the low concentration portion of the chromatographic zone the partial vapor pressure was proportional to the concentration of the fatty acid, in the high concentration portion of the zone dimerization occurred and the partial vapor pressure was proportional to the square root of the concentration. This explained the observed zone shape. The idea was born of incorporating in the stationary phase a substance which would itself interact with the solute molecules to form dimers at all concentrations, and so revert to the condition that the distribution coefficient was independent of concentration. Thus, stearic acid was incorporated in the stationary phase and we found fairly quickly that the best stationary phase for the separation of the short chain acids was a solution of stearic acid in a silicone oil. I have gathered from other workers that they have spent many years searching for better stationary phases and so far as I know only one alternative has yet been produced.

Having got the columns to operate properly, we then proceeded to go into a more detailed consideration of the theory. I say "we." My major function in development of the theory was adding up the sums and seeing that they gave the right answer because Dr. Martin, though an excellent operator of higher mathematics, has always been extremely poor in adding up (and rather weak on dividing too, I may say). He has confessed to me on many occasions that he is often out by a factor of ten—but usually on the right side.

The next development was to get a more convenient device for titrating; and so the design was produced for the recording burette. This simple instrument worked extremely well; I used to sit in front of it, turning the handle and carefully watching the color of the indicator in the cell. We were able to plot automatically the zones as titration proceeded and to elucidate the effect of some column parameters such as pressure drop.

This apparatus had certain disadvantages. If anyone came into talk to you and you took your eye off the titration cell, a zone would emerge that would be missed, and so spoil the record. An automatic recording burette was then devised by putting a photocell against the titration cell and so actuating the recording burette when the indicator color changed. This was the first automatic recording gas chromatogram.

From there on the pathway seemed clear. The work was extended to study column behavior in terms of interaction between solute and stationary phase. We continued with aliphatic amines, and came up with the idea of using two stationary phases and plotting retention times to get an indication of the chemical structure of the amine. We were able, by use of two columns, to define an unknown amine as primary, secondary, or tertiary.

Then came the problem of designing a general detector. Dr. Martin at that time was perfectly well aware of the thermal conductivity cell, as he is aware of most scientific instruments, but he felt that the inherent flow sensitivity of the designs that had so far been produced made them unattractive. I know that for some years he had been thinking about the gas density meter. At first, however, he made an attempt to make a mass recording detector. He spent some time making minute microbalances from quartz, but unfortunately these were so difficult to make and so fragile that they could be made only for a short period each day. He was hoping to condense out the vaporized material onto a cold balance pan and record automatically the mass of the material. This did not, in the long run, work out, and during this time I am sure he was still thinking about the gas density meter.

While the work was going on with the balance, I was doing more work with the titration system, studying the behavior of aromatic amines. This showed that with aromatic derivatives the picture of solute-solvent interaction becomes more complex owing to ring effects and positional isomerism. But at least this did extend the range to weak bases by titrating in glacial acetic acid with perchloric acid using the same instrument as before.

At this time, as Dr. Martin has told you, Ray visited our laboratory and then did some excellent early work at I.C.I. using a catharometer. Meanwhile, Martin was becoming less interested in mass and reverted to the gas density meter. As usual, he spent a long time thinking. First he made a glass model, to demonstrate the general principle, not being interested in sensitivity, and it worked. He then made a small brass instrument and again that worked. The first full-scale model I still have and still use. This instrument immediately opened up the field for ourselves and we began then to study the behavior of a much wider range of compounds.

First we chose the saturated paraffin hydrocarbons and so needed pure standard hydrocarbons. The source was the stock held for the country by Dr. Birch at what was then Anglo-Iranian and is now British Petroleum. I wrote to Dr. Birch and asked for some samples; they wrote back very promptly and said they were very happy to let us have them, but were mildly interested in why we wanted such a wide range of structures. I sent them, in return, some early gas chromatograms of separations of the components of petroleum ethers. Dr. Birch and Mr. Desty arrived the next day; British Petroleum never was a company to let any dust grow under its feet. From then on, Desty and Harborn and their collaborators have done much excellent work in this field. They were, I think, outside ourselves, the first people ever to construct and use a gas density meter.

We did some work with a large-scale column many years ago, 20 ft long and an inch in diameter and we found, in the standards of those days of column efficiency, that there was no great drop in efficiency per foot. Dr. Martin designed a catharometer cell which was much less flow sensitive than the conventional direct flow type and we used this on the large columns. At the time we were interested, in conjunction with Dr. Tatlow in Birmingham, in the separation of fluorocarbons. But Dr. Tatlow developed his own column so quickly that they carried on very effectively on their own and were the first to publish on the subject of large-scale columns.

Having the gas density meter and having separated a series of alcohols, ketones, etc., we published general articles on the technique in a few journals. This began to stir up much more widespread interest. At that time we were in the position of knowing more about the subject than anybody else. During the next few years we had through our laboratory many people interested or who had already started work in this field, and we both had an extremely interesting time.

But always both of us were interested in the use of the chromatogram for getting physicochemical data on the way molecules interact in solution.

The gas chromatogram has now provided enough information on the types of intermolecular attraction to give more insight into the behavior of liquid-liquid chromatograms.

From then on the technique spread very widely. There is always a time lag between spread of a technique in Britain and its spread in the United States. Somebody has said that there is nothing shyer than a million dollars, but our experience would suggest that there is nothing more resistant to somebody else's ideas than a scientist. This is possibly the reason why the initial suggestion of the gas chromatogram was never taken up. The only detectors then available commercially were the various types of catharometers. The gas density meter was also beginning to be available.

After the initial development of the technique and its general trends were clear, Dr. Martin decided to leave the Medical Research Council and connect himself more directly with industry and to do consultant work. At that time I turned my attention to the long chain fatty acids. The first paper Dr. Martin and I wrote together was that on the separation of the short chain fatty acids, and our last paper was on the long chain fatty acids. I was attracted to these substances because of their intractibility. Proteins are bad enough, but at least they are soluble in water. Although fat-soluble substances were the first compounds to be studied chromatographically because of their low water solubility, methods of separation were not highly developed except for the reversed phase liquid-liquid chromatogram, which Martin had developed at the Lister Institute.

After Martin had left the National Institute, I carried on working in this field of separation of the long chain acids and applied the technique to a variety of problems. I became interested in the lipids of human blood, and Dr. Lovelock, a physical chemist who worked in the field of blood coagulation and fragility of red cells, and I began to collaborate. We examined the fatty acids of blood and then were drawn into work on coronary artery disease. One of the problems we came up against was the fact that often only small blood samples were available, so that we were working at the limit of the sensitivity of the gas density meter. Dr. Lovelock and I discussed the need for a more sensitive detector, and he said he thought he could make such a device. He then developed the argon ionization cell and we were able to extend our work by virtue of the much lower loads that we could apply to the column.

From now on, development of the technique became extremely rapid Dr. Golay later worked out the theory of the capillary column and proceeded, unlike more theoriticians, to practical demonstration. Capillary columns are essential in the petroleum hydrocarbon field where mixtures of almost every conceivable type of carbon skeleton exist and separation factors are often very small. High plate numbers have to be used to get useful separations. For many other fields where large separation factors can often be used, it would be more advantageous to run capillary columns at much higher flow rates and lower efficiencies. Much faster separations can then be carried out.

This raises the whole problem of the recording and presenting of information. Most people are wedded to the concentration-time plots, but this is one of the less useful ways of presenting the data because one always has the problem of measuring some function of peak width. When dealing with very narrow peaks emerging at high speed in order to get measurable distances, high paper speeds have to be used. This may, if one works at very high speeds, introduce uncertainties in paper movement. It is simpler not to plot concentrations but the integral record as a series of steps. Time is no longer of concern as a function for calculation of peak areas. From such diagrams just as much information can be obtained as from the conventional peaks.

Other auxiliary information is often required such as the measurement of radioactivity of substances eluted from the chromatogram. In England, Popjak has developed a simple cell, attached to the outlet of a gas density meter, in which a scintillator is contained in solution in a solvent such as toluene The gas stream is arranged to bubble through the cell so that the peaks are absorbed. The cell is strapped between two photomultipliers, in this way count rate can be plotted automatically simultaneously with the record from the vapor detector. This enables one to determine directly the specific activities of the labeled materials. An alternative method is to use a proportional flow counter, at the outlet of the vapor detector.

It is interesting, to compare the development of gas chromatography, in so far as the commercial instrument houses are concerned, with the present status of spectrophotometry. Originally, all spectrophotometers were designed and operated in academic or industrial laboratories. Nowadays the development of spectrophotometers is carried out almost exclusively within the instrument industries of this country, Great Britian and Germany. The commercial houses, rather than academic laboratories, produce the new instruments. This is the sort of thing that is going to happen with the gas chromatogram. Up until now the development of new detectors and columns has been carried out in academic research institutes or in industry. Now that the instrument companies are becoming much more closely involved, they will produce their own designs.

The capillary column has gone on from strength to strength. In Britain, Desty and his co-workers at British Petroleum have designed a very ingenious apparatus for drawing glass tubing to form glass capillaries of any desired bore, and have been able to attain something of the order of three quarters of a million theoretical plates, largely due, it is thought, to the very smooth bore. These capillary tubes enable one to deposit a very even thin film of the stationary phase. On the other hand, Scott of Benzole Producers, has used plastic tubing, again with a much smoother bore than metal columns, and has attained the same order of efficiency--750,000 theoretical plates.

Another interesting development which has been going on in the last few years is a much greater theoretical understanding of the operation of the gas chromatogram. Earlier theoretical papers (except the original theoretical plate treatment of Martin and Synge) were so difficult to handle mathematically and used many parameters devoid of physical meaning, that they were rarely of practical use to chromatographers. Now this has changed. Dr. Glueckauf recently presented a very elegant paper on the theory of separation of highly radioactive gases in which the heat evolved by these gases effected desorption from the adsorbent. He also correlated theory and practice in a very elegant manner. The same is true of Dr. Golay and also the Shell Group (Van Deemter, etc.).

The work on large-scale columns which has gone on in the last few years has again culminated in the production of commercial models There still are differences of opinion on the way these columns should be constructed. During the next few years experience will show whether it is better to have a number of parallel small columns or a single wide column. Now that the instrument companies have a direct interest in this they will find out very quickly which is the best method—they have to sell the instruments.

Automatic fraction collectors are still in their infancy. A simple detector which can be used to operate a relay to change collectors has yet to be produced. For many workers, and particularly for chemical laboratories who are not interested in the fine details of chromatographic separations or even in seeing the record, there is something to be said for a much cheaper large-scale column in which there is no recording of the separation but merely some visual indication of an emerging zone.

Development is now proceeding along very different lines for industrial and research instruments. We have high speed, high sensitivity, low load, automatic machines for analysis but we also need milligram level columns for research studies, particularly for radioactive work.

By using large-scale columns the chemical suppliers should now be able to supply us with highly pure chemicals. I remember when the paper chromatogram was developed for separations of the amino acids, many chemical suppliers were distressed to get rude letters from their customers, saying, for example, that the material supplied as l-glutamic acid, in the first place, was not l- and in the second place was not glutamic acid. Obviously, the same thing has been happening in the last few years with the chemical suppliers with regard to the more volatile substances with which we can deal.

Dr. Lipsky has spoken about his separations of sterols on the gas chromatograph. This is a field in which I am particularly interested, since it is likely to open up new avenues of attack on various biochemical and chemical problems involving the metabolism of lipids. Although I myself don't think cholesterol has much to do with the coronary artery disease, a large number of other people do, and they, I am sure, will be very happy to measure cholesterol with the gas chromatogram instead of by conventional techniques.

I have tried to outline the way in which the first idea of the gas-liquid chromatogram, occurring as a few lines in a general paper on liquid-liquid chromatography, has developed since its inception. It has grown into a technique of tremendous ramification (not the least of which is making money for the instrument companies), still not yet fully exploited. There is much left to do, so the next few years will be intensely interesting.

CHAPTER XXIV

Rapid Chromatographic Separation and Determination of Helium-Neon-Hydrogen and Nitrogen-Krypton-Methane Mixtures and Determination of Argon in the Presence of Oxygen at Room Temperature

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Activated charcoal (*2–4*, *7*, *8*, *11*, *12*, *14*, *15*), silical gel, (*5*, *16*), aluminium-silicate molecular sieves (*1*, *4*, *6*, *13*), and mixtures of various adsorbents (*6*) have been used for the chromatographic separation of rare gases (*4*, *7*), rare gases mixed with permanent gases (*1*, *4–6*, *11–13*, *15*, *16*), and mixtures of rare gases, permanent gases, and gaseous hydrocarbons (*4*, *8*, *11*, *14*). Special analytical studies have been made on the separation of isotopes of gases (*2*), radioactive rare gas isotopes (*3*), and the determination of small quantities of rare gases (*5*, *11*, *12*).

From the results of these studies it is evident that the practical anallysis of the following mixtures—helium, neon, and hydrogen; argon and oxygen; nitrogen, krypton, and methane—has not been solved. Helium mixed with neon (without the determination of hydrogen) can be separated only at low temperatures (*4*, *8*, *14*). Argon can be separated from oxygen only partially using 5A Linde molecular sieve with an unspecified amount of water (*6*, *13*) (which plays a deciding role in the sorption properties of the molecular sieve towards permanent gases) (*9*, *10*). It is possible to avoid these difficulties in the separation by a preliminary elimination of oxygen (*5*). A similar situation exists in the case of the krypton-methane mixture (*4*, *12*).

In this paper the conditions will be discussed under which the above-mentioned problems can be solved at room temperatures.

EXPERIMENTAL

A conventional gas chromatograph was used for this work. Platinum thermal conductivity cells kept at 22° C served as the detector. In the separation of the helium-neon-hydrogen mixture, argon was used as the carrier gas, in the determination of argon and in the separation of the krypton-methane mixture, hydrogen was used as the carrier gas. Activated calcium aluminium silicate, ($CaO \cdot Al_2O_3 \cdot 2\ SiO_2$) (5A Linde Molecular Sieve) (*10*) and activated charcoal Supersorbon of grain size 0.2–0.4 mm were used as adsorbents. The chromatographic columns were aluminium tubes of required length (see below), with a 7-mm ID. In all cases, a constant volume of variable amounts of the gas sample diluted with the carrier gas was fed by injection.

SEPARATION OF HELIUM-NEON-HYDROGEN MIXTURE

On a column packed with 109 g of activated 5A Linde Molecular Sieve, hydrogen can be completely separated from helium and neon, and helium separated sufficiently from neon at 22° C. The same column, at the temperature of dry ice, completely separates the helium neon pair (Fig. 1). The specific retention volumes (chromatographic spectra) can be seen in Table I. The dependence of the value $U_g{}^0$ (which corresponds to the value $V_g{}^0$ in gas-liquid chromatography) upon the reciprocal temperature can be seen in Fig. 2. The relation is not linear as it is in the case of gases of higher adsorption energy (*10*) (oxygen, nitrogen, methane, carbon

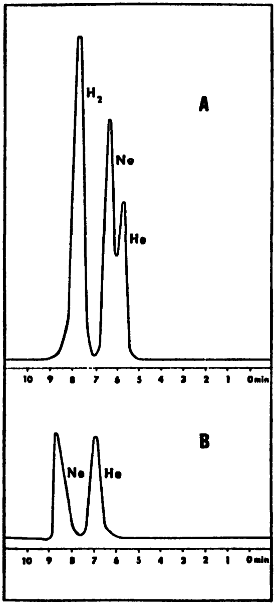

FIG 1 Chromatographic separation of helium-neon-hydrogen mixture on calcium aluminum silicate (Linde Molecular Sieve 5A) (A) Temperature: 22° C; carrier gas: 0.5 ml A/sec. (B) Temperature: −78° C; carrier gas: 0.89 ml A/sec.

TABLE I

SPECIFIC RETENTION VOLUMES (CHROMATOGRAPHIC SPECTRA)

Component	t_{max}	$t_{max} - t_0$	U_g^0
Helium	342	0	0.000
Neon	381	39	0.150
Hydrogen	467	125	0.485
Oxygen[11]	—	—	4.44
Nitrogen[11]	—	—	13 3

NOTE. Temperature, 20° C; 109 g Linde Molecular Sieve 5A; grain size, 0.2–0.4 mm activated at 400° C; carrier gas, argon 0.5 ml/sec; inlet pressure, 1013 tor; compressibility factor 0 786

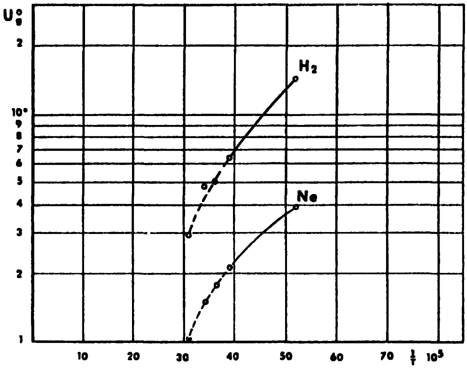

FIG 2 Dependence of log U_g^0 for neon and hydrogen on the reciprocal temperature (for dead volume estimation served U_{max} of helium).

monoxide); this suggests that in the separation of these components other factors besides sorption play a role, i.e., diffusion.

The calibration curves for helium, neon, and hydrogen are linear in amounts over 10 μl gas (calibration by measuring the peak areas will give better results then that from the peak heights). This analysis takes 10 minutes.

DETERMINATION OF ARGON MIXED WITH OXYGEN

Argon is separated from other permanent gases in the chromatograph on active molecular sieve, type 5A, in one fraction along with the oxygen. When hydrogen is used as a carrier gas, oxygen is eliminated quantitatively from the mixture at room temperature on a catalytic precolumn (palladium carried on a support).

PREPARATION OF THE CATALYST

The palladium was carried on to the supporting material, such as aluminium silicates or Celite, in the form of ammonia complex; 2 ml of 10% water solution of palladium chloride (0.12g Pd) was settled by means of 36% ammonia. A white precipitate—Pd $(NH_3)_2Cl_2$—was formed. The suspension was made up to 100 ml with the same ammonia. Owing to the excess of ammonia, the complex was resolved after some hours upon formation of $(Pd(NH_3)_4)^{++}$.

Into the solution prepared in such a way 40 g of dried support was added. The suspension formed is transferred into a flask and heated with continuous evacuation until dry. The dry product is then packed in a metal or glass tube, purged with hydrogen, and the column moved slowly through an oven heated to 500° C in the direction of the hydrogen stream along the whole column. The palladium catalyst will turn gray as it is reduced.

The calibration curve, according to peak areas, and according to peak heights, is linear in the usual range. It is possible to calibrate for small amounts of argon before the analysis by determining argon in the air.

TABLE II

QUANTITATIVE ELIMINATION OF OXYGEN BY MEANS OF CATALYTIC PRECOLUMN

Argon, ml	Oxygen, ml	Peak area for A, mm^2	Error, %
0.00	0.10	0	0.00
0.00	0.50	0	0.00
0.00	1.00	0	0.00
0.00	2.00	0	0.00
0.00	3.00	0	0.00
0.00	4.00	0	0.00
0.00	5.00	0	0.00
0.50	0.00	255	+2.82
0.50	0.50	244	−1.61
0.50	0.50	244	−1.61
0.60	0.00	385	+4.34
0.60	2.00	364	−1.35
0.60	1.00	382	−3.53
0.60	4.40	356	−3.53
0.60	0.00	360	−2.44
2.00	0.00	1110	+4.18
2.00	1.00	1055	−1.86
2.00	0.60	1057	−1.67
		Average error	±2.88%
		Average error of sampling	±2.00%

NOTE: ID 6 mm; 0.019 g Pd in 0.3% on the support.

The quantitative elimination of oxygen was followed by adding electrolytic oxygen, in volumes of 0.10–5.00 ml mixed in various ratios, to the argon (see Table II). The catalytic precolumn, ID 6 mm, contained 0.019 g Pd in a concentration of 0.3 % on the support. The catalytic elimination of the oxygen was complete even at the volume rate of 2.8 Nml H_2/sec which corresponds to the linear stream velocity of 165 cm/sec and to the contact time of 22 sec over 1 g Pd. The catalytic properties of the palladium precolumn are not influenced by the presence of water formed by the reaction of 250 ml oxygen fed on to the column. An example of the determination of air, argon, and of the analysis of a recycling gas from an ammonia synthesis is given in Fig. 3. The analysis takes 2 to 5 minutes.

SEPARATION OF THE NITROGEN-KRYPTON-METHANE MIXTURE

The chromatographic spectra from activated charcoal and calcium aluminum silicate (Table III) show that, at room temperatures, krypton can be separated from nitrogen on a molecular sieve (cf. *4*) only with difficulty, whereas it separates cleanly on activated charcoal. Although on this adsorbent a clean separation of the krypton-methane mixture meets with difficulty, it can easily be performed on zeolite. From the chromatographic spectra, it is possible to calculate the composition of the mixed adsorbent

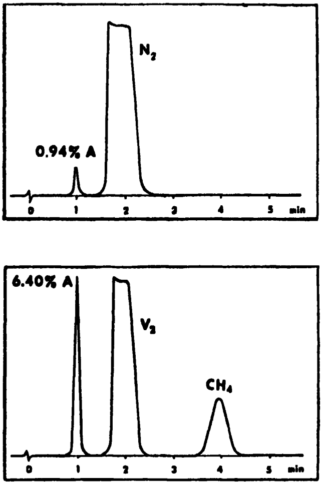

FIG. 3. Chromatographic determination of argon in air and in recycling gas from ammonia synthesis.

TABLE III

SPECIFIC RETENTION VOLUMES (CHROMATOGRAPHIC SPECTRA) OF NITROGEN, KRYPTON, AND METHANE ON CHARCOAL AND MOLECULAR SIEVE 5A

	Charcoal	Molecular sieve 5A (*11*), water content, 2 % w
Temperature, ° C	20	20
Grain size, mm	0.2–0.4	0.2–0.4
Carrier gas, hydrogen ml/sec	2.88	1.29
Inlet pressure, tor	763	591
Outlet pressure, tor	748	476
Adsorbent weight, g	8.8	18.3
Specific retention volumes, U_g^0		
Nitrogen	8.1	8.84
Krypton	48	8.8
Methane	48	16.6

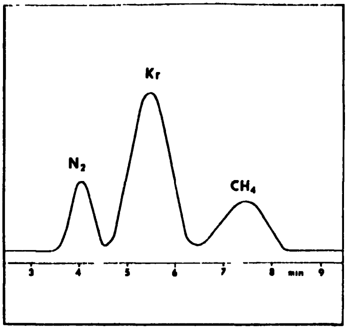

FIG. 4. Chromatographic separation of nitrogen-krypton-methane mixture on mixed adsorbent (charcoal and Linde Molecular Sieve 5A, 1:10).

TABLE IV

COMPARISON OF CALCULATED AND FOUND SPECIFIC RETENTION VOLUMES ON MIXED ADSORBENT

Compound	U_g^0, calculated	U_g^0, found
Nitrogen	8.8	9.1
Krypton	12.4	13.2
Methane	19.5	18.9

NOTE: Charcoal: Linde Molecular Sieve 5A = 9.3:90.7.

which will separate krypton from the components mentioned. For example:

$$U_g^0 = \frac{X_A U_g^0 + Y_B U_g^0}{100}$$

where X and Y are per cents by weight of both adsorbents and ${}_AU_g^0$ is the respective specific retention volume. Figure 4 illustrates this separation and Table IV shows the conformity of the values of U_g^0 calculated with those found using mixed adsorbents. The analysis takes 5 to 9 minutes.

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CHAPTER XXV

Comparative Retention Values of Representative Sample Types on Standard Gas Chromatography Columns

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INTRODUCTION

For some time, there has been a need for tables of retention values in order to predict the applicability of a particular column to a particular problem in gas chromatography. At the New York American Chemical Society's meeting in September, 1957, H. M. Tenney of Esso Research Laboratories, Baton Rouge, Louisiana, outlined a procedure for obtaining the maximum amount of information concerning the selectivity of various liquid substrates in the minimum amount of time (*1*). Subsequent to Tenney's work, James (*2*) and Raupp (*3*) have published useful compilations of retention data.

For this particular study, eighteen standard mixes representing a wide variety of chemical types were run on a group of the most commonly used Perkin-Elmer partition columns; namely Types A, B, C, K, O, P, Q, and R, at a temperature of 100°C. The first eight mixes (light hydrocarbons) were run in addition at a temperature of 50°C.

All columns were specially prepared for this investigation, conforming to the latest production specifications. The liquid substrate was put on 60–80 mesh Chromosorb R at a concentration of 20% by weight. The column inlet pressure was adjusted to give a flow rate of 40 to 100 ml/min, measured at room temperature.

In addition, supplementary tables give retention data for two applications of particular interest: light hydrocarbon analysis on an E column (dimethylsulfolane) at 50°C, and analysis of fatty acid methyl esters on a P column at 210°C.

HOW TO USE THE DATA

The tables for each column list in order from left to right the mix number, component name, boiling point, pressure in pounds per square inch gage and flow rate in milliliters per minute of helium (*P*/*F*), net retention time measured from the air peak (the retention time given for air is that measured from the start), and finally, the ratio of the net retention time of the component to that of *n*-pentane under the same conditions.

These relative retention ratios are pure numbers independent of column length, flow rate, and ratio of substrate to inert support. Only the column temperature and the nature of the substrate need by specified. By measuring experimentally the net retention time for *n*-pentane through a particular column under any given set of conditions but *at the same temperature*, the ratios may be used to compute the net retention times for all the other components listed, thus:

$$t_r - R_p t_p$$

where t_r = net retention time for component x; R_p = tabulated *n*-pentane ratio for component x; t_p = net retention time for *n*-pentane measured from the air peak. Sometimes the retention time for the start of injection is used in such computations. This is unsound because the ratios obtained, whether in relation to air or carrier gas (R_f values) or in relation to some other standard substance, become dependent on the ratio of liquid substrate present on the column to the solid support.

The graphs, two for each column, consist of plots of retention ratios at 100° C vs the boiling points of standard mixture components boiling between 20° and 145°C. Each curve is labeled with the mix number. Each mix also has its identifiable plotting points making it possible to locate a specific compound by noting its boiling point on the proper mix line.

Much qualitative information concerning the separation characteristics of a column can be obtained at a glance. The farther apart two or more curves are the better the separation by chemical type. For example, on a K column, normal paraffins boiling up to about 160°C will emerge prior to benzene (b.p. 80°C), the lowest boiling member of the aromatic series. On the other hand, it is sometimes desirable to have a nonselective straight boiling point separator, in which case one looks for the appropriate mix curves close together or overlapping. Squalane (column U) is such a nonselective, straight boiling point separator for hydrocarbons (*1*). Lastly, the flatter the slope of a curve the greater will be the separation with a homologous chemical type.

The selection of the best column for a particular application is still largely an empirical art. If the constituents of a sample are known, then it is possible to make use of published retention data as a guide. Properly used, such tables and graphs mean a considerable saving of time and effort. It is hoped that the data presented here will be useful to other groups working in the field of gas chromatography.

TABLE I

STANDARD MIXES USED IN COLUMN STUDY

Mix No	Chemical Type	Graph Symbol
1	C_1–C_4 *n*-paraffins	○
2	C_5–C_8 *n*-paraffins	×
3	2-Methyl paraffins	
4	C_2–C_4 olefins	
5	1-Alkenes	△
6	2-Alkenes	□
7	Diolefins	
8	Acetylenes	
9	Alkyl benzenes	○
10	Cyclopentanes	×
11	Cyclohexanes	△
12	Primary alcohols	○
13	Secondary alcohols	×
14	Tertiary alcohols	△
15	Aldehydes	○
16	Ketones	×
17	Acetates	△
18	Ethers	□

RETENTION DATA, COLUMN A

Diisodecyl phthalate, 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature· 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (Air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	25/92	0.00	0.00
	Ethane	−89	25/92	0.20	0.04
	Propane	−42	25/92	0.65	0.12
	Butane	−0.5	25/92	2.00	0.35
2	Pentane	+36	25/92	5.65	1.00
	Hexane	+69	25/92	15.3	2.71
	Heptane	+98	25/92	40.1	7.10
	Octane	+126	25/92	—	—
3	2-Methylpropane	−12	25/92	1.40	0.25
	2-Methylbutane	+28	25/92	4.40	0.78
	2-Methylpentane	+60	25/92	11.8	2.09
4	Ethylene	−104	25/92	0.20	0.04
	Propylene	−48	25/92	0.80	0.14
	Isobutane	−6.9	25/92	2.15	0.38
	Butene-1	−6.3	25/92	2.15	0.38
	trans-Butene-2	+0.9	25/92	2.80	0.50
	cis-Butene-2	+3.7	25/92	3.10	0.55
5	Pentene-1	+30.0	25/90	5.70	1.01
	Hexene-1	+63.5	25/90	16.2	2.87
6	*trans*-Pentene-2	+36.3	25/90	7.00	1.24
	cis-Pentene-2	+36.9	25/90	7.40	1.31
	trans-Hexene-2	+67.9	25/90	17.9	3.17
	cis-Hexene-2	+68.8	25/90	19.9	3.52
7	Propadiene	−34	25/92	1.40	0.25
	Butadiene-1,3	−4	25/92	2.80	0.50
	2-Methylbutadiene-1,3	+34	25/92	8.25	1.46
8	Acetylene	−84	25/88	0.35	0.06
	Propyne	−23	25/88	1.60	0.28
	Butyne-1	+8	25/88	3.65	0.65
Misc.	Air	—	25/92	(1.10)	0.00
	Carbon monoxide	−190	25/92	0.00	0.00
	Carbon dioxide	−78	25/92	0.20	0.04
	Neopentane	+10	25/92	2.35	0.41
	Isooctane	+99	25/92	39.6	7.01

RETENTION DATA, COLUMN A—*Continued*

Diisodecyl phthalate, 20% by weight on 60–80 mesh Chromosorb; length 4 meters, temperature: 100° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
1	Methane	−162	25/70	0.00	0.00
	Ethane	−89	25/70	0.15	0.07
	Propane	−42	25/70	0.40	0.19
	Butane	−0.5	25/70	1.00	0.48
2	Pentane	+36	25/70	2.10	1.00
	Hexane	+69	25/70	4.80	2.29
	Heptane	+98	25/70	10.8	5.14
	Octane	+126	25/70	23.4	11.1
3	2-Methylpropane	−12	25/70	0.80	0.38
	2-Methylbutane	+28	25/70	1.70	0.81
	2-Methylpentane	+60	25/70	3.75	1.78
4	Ethylene	−104	25/70	0.15	0.07
	Propylene	−48	25/70	0.45	0.21
	Isobutene	−6.9	25/70	1.05	0.50
	Butene-1	−6.3	25/70	1.05	0.50
	trans-Butene-2	+0.9	25/70	1.30	0.62
	cis-Butene-2	+3.7	25/70	1.40	0.67
5	Pentene-1	+30.0	25/70	2.05	0.98
	Hexene-1	+63.5	25/70	4.80	2.29
6	*trans*-Pentene-2	+36.3	25/70	2.25	1.07
	cis-Pentene-2	+36.9	25/70	2.40	1.14
	trans-Hexene-2	+67.9	25/70	5.30	2.52
	cis-Hexene-2	+68.8	25/70	5.60	2.67
7	Propadiene	−34	25/70	0.75	0.35
	Butadiene-1,3	−4	25/70	1.30	0.62
	2-Methylbutadiene-1,3	+34	25/70	2.80	1.33
8	Acetylene	−84	25/70	0.25	0.12
	Propyne	−23	25/70	0.80	0.38
	Butyne-1	+8	25/70	1.55	0.74
9	Benzene	+80	25/70	12.9	6.14
	Toluene	+111	25/70	29.9	14.2
	Ethylbenzene	+136	25/70	58.4	27.8
	p-Xylene	+138.4	25/70	66.3	31.6
	m-Xylene	+139.1	25/70	66.3	31.6
	o-Xylene	+144.4	25/70	80.0	38.1
	Isopropylbenzene	+152	25/70	90.8	43.2

RETENTION DATA, COLUMN A—*Continued.*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
10	Cyclopentane	+49	25/70	4.00	1.90
	Methylcyclopentane	+72	25/70	6.65	3.17
11	Cyclohexane	+81	25/70	9.3	4.90
	Methylcyclohexane	+101	25/70	15.8	7.52
12	Methanol	+65	20/54	3.6	1.38
	Ethanol	+78	20/54	4.8	1.85
	Propanol	+97	20/54	10.4	4.00
	Butanol	+118	20/54	24.0	9.24
13	2-Propanol	+82	25/70	4.9	2.33
	2-Butanol	+100	25/70	11.0	5.24
14	*tert*-Butyl alcohol	+83	25/70	5.6	2.67
	tert-Amyl alcohol	+102	25/70	14.1	6.71
15	Acetaldehyde	+20	25/70	2.0	0.95
	Propionaldehyde	+50	25/70	3.9	1.86
	Butyraldehyde	+75	25/70	8.2	3.90
	Valeraldehyde	+103	25/70	18.2	8.67
16	Acetone	+56	25/70	4.4	2.10
	2-Butanone	+80	25/70	9.0	4.29
	2-Pentanone	+103	25/70	17.3	8.24
	2-Heptanone	+150	25/70	76.0	13.6
17	Methyl acetate	+58	25/70	4.5	2.14
	Ethyl acetate	+77	25/70	7.7	3.67
	n-Propyl acetate	+102	25/70	15.9	7.57
	n-Butyl acetate	+126	25/70	33.4	15.9
18	Diethyl ether	+35	25/70	2.6	1.24
	Diisopropyl ether	+68	25/70	5.2	2.48
	Di-*n*-butyl ether	+138	25/70	44.0	20.9
Misc	Air	—	25/70	(1.10)	0.00
	Carbon monoxide	−190	25/70	0.00	0.00
	Carbon dioxide	−78	25/70	0.15	0.07
	Neopentane	+10	25/70	1.10	0.52
	Isooctane	+99	25/70	10.1	4.81
	Water	+100	25/70	6.4	3.04

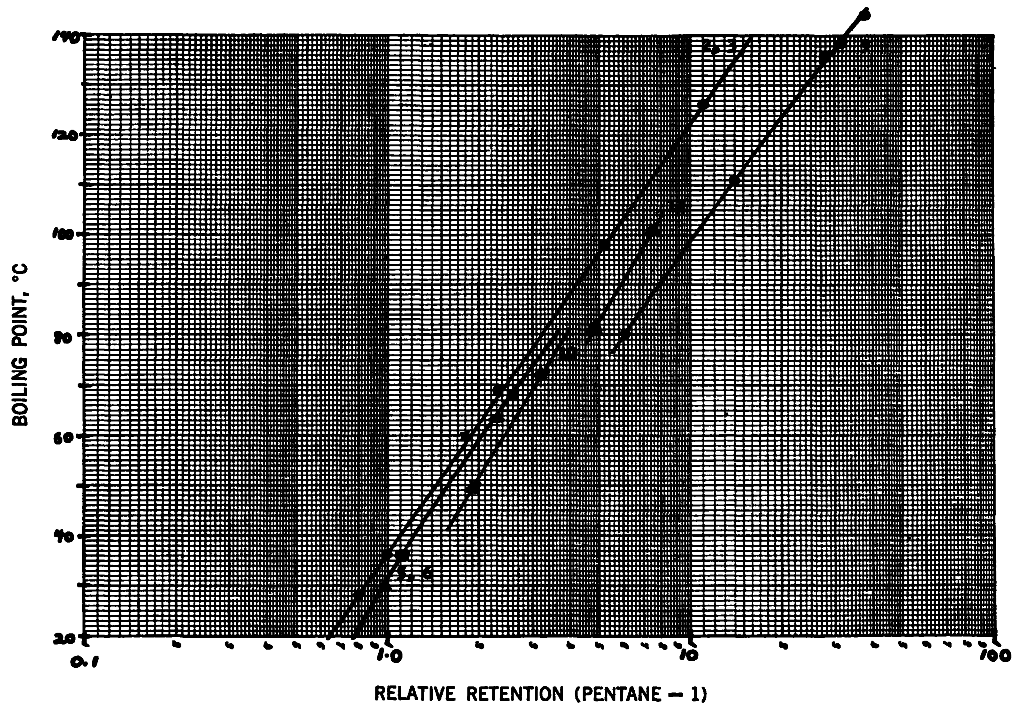

FIG. 1. Separation of hydrocarbons on diisodecyl phthalate (A) at 100° C.

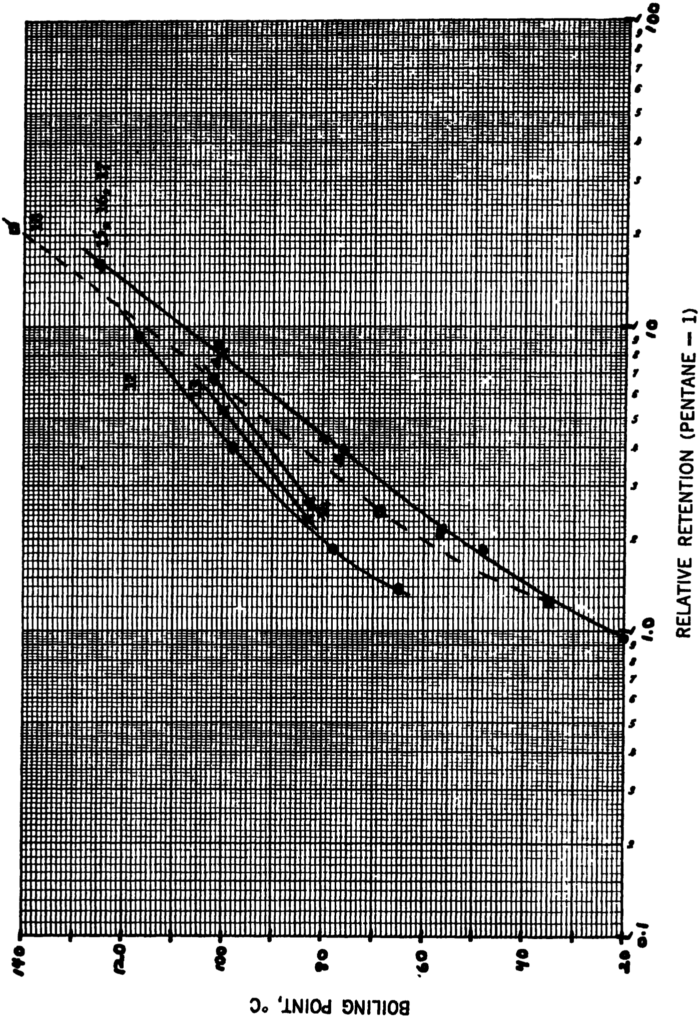

Fig 2 Separation of oxygenated compounds on diisodecyl phthalate (A) at 100° C.

RETENTION DATA, COLUMN B

Di-2-ethylhexyl sebacate, 20% by weight on 60–80 mesh Chromosorb; length, 4 meters, temperature 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio ($n\mathrm{C}_5$ = 1)
1	Methane	−162	20/62	0.00	0.00
	Ethane	−89	20/62	0.35	0.04
	Propane	−42	20/62	1.20	0.12
	Butane	−0.5	20/62	3.70	0.36
2	Pentane	+36	20/62	10.40	1.00
	Hexane	+69	20/62	30.0	2.88
	Heptane	+98	20/62	77.2	7.42
	Octane	+126	20/62	199.0	19.1
3	2-Methylpropane	−12	20/62	2.60	0.25
	2-Methylbutane	+28	20/62	8.05	0.77
	2-Methylpentane	+60	20/62	21.2	2.04
4	Ethylene	−104	20/62	0.35	0.04
	Propylene	−48	20/62	1.30	0.13
	Isobutene	−6.9	20/62	3.80	0.37
	Butene-1	−6.3	20/62	3.80	0.37
	trans-Butene-2	+0.9	20/62	4.85	0.47
	cis-Butene-2	+3.7	20/62	5.40	0.52
5	Pentene-1	+30.0	20/62	10.3	0.99
	Hexene-1	+63.5	20/62	28.6	2.75
6	*trans*-Pentene-2	+36.3	20/62	12.5	1.20
	cis-Pentene-2	+36.9	20/62	13.3	1.28
	trans-Hexene-2	+67.9	20/62	32.4	3.12
	cis-Hexene-2	+68.8	20/62	35.4	3.40
7	Propadiene	−34	20/62	2.40	0.23
	Butadiene-1,3	−4	20/62	5.00	0.48
	2-Methylbutadiene-1,3	+34	20/62	14.95	1.44
8	Acetylene	−84	20/62	0.65	0.06
	Propyne	−23	20/62	2.10	0.20
	Butyne-1	+8	20/62	6.35	0.61
Misc.	Air	—	20/62	(1.35)	0.00
	Carbon monoxide	−190	20/62	0.00	0.00
	Carbon dioxide	−78	20/62	0.35	0.04
	Neopentane	+10	20/62	4.10	0.39
	Isooctane	+99	20/62	70.0	6.73

RETENTION DATA, COLUMN B—*Continued*

Di-2-ethylhexyl sebacate, 20% by weight on 60–80 mesh Chromosorb; length: 4 meters, temperature: 100° C.

Mix no	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
1	Methane	−162	20/48	0.00	0.00
	Ethane	−89	20/48	0.30	0.08
	Propane	−42	20/48	0.70	0.19
	Butane	−0.5	20/48	1.80	0.49
2	Pentane	+36	20/48	3.70	1.00
	Hexane	+69	20/48	8.40	2.27
	Heptane	+98	20/48	18.4	4.97
	Octane	+126	20/48	38.9	10.5
3	2-Methylpropane	−12	20/48	1.35	0.37
	2-Methylbutane	+28	20/48	3.05	0.83
	2-Methylpentane	+60	20/48	6.60	1.78
4	Ethylene	−104	20/48	0.20	0.05
	Propylene	−48	20/48	0.75	0.20
	Isobutene	−6.9	20/48	1.80	0.49
	Butene-1	−6.3	20/48	1.80	0.49
	trans-Butene-2	+0.9	20/48	2.20	0.60
	cis-Butene-2	+3.7	20/48	2.35	0.64
5	Pentene-1	+30.0	20/48	3.95	1.04
	Hexene-1	+63.5	20/48	8.45	2.28
6	*trans*-pentene-2	+36.3	20/48	4.25	1.15
	cis-Pentene-2	+36.9	20/48	4.75	1.28
	trans-Hexene-2	+67.9	20/48	9.40	2.54
	cis-Hexene-2	68.8	20/48	10.0	2.70
7	Propadiene	−34	20/48	1.35	0.37
	Butadiene-1,3	−4	20/48	2.30	0.62
	2-Methylbutadiene-1,3	+34	20/48	5.00	1.35
8	Acetylene	−84	20/48	0.40	0.11
	Propyne	−23	20/48	1.50	0.41
	Butyne-1	+8	20/48	2.60	0.70
9	Benzene	+80	20/48	21.3	5.61
	Toluene	+111	20/48	46.9	12.3
	Ethylbenzene	+136	20/48	90.8	23.9
	p-Xylene	+138.4	20/48	101.7	26.8
	m-Xylene	+139.1	20/48	101.7	26.8
	o-Xylene	+144.4	20/48	121.7	32.0
	Isopropylbenzene	+152	20/48	139.4	36.7

RETENTION DATA, COLUMN B—*Continued.*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio ($n\mathrm{C}_5$ = 1)
10	Cyclopentane	49	20/48	7.0	1.84
	Methylcyclopentane	72	20/48	11.5	3.03
11	Cyclohexane	+81	20/48	15.4	4.07
	Methylcyclohexane	+101	20/48	25.5	6.71
12	Methanol	+65	20/50	4.5	1.18
	Ethanol	+78	20/50	6.2	1.63
	Propanol	+97	20/50	14.1	3.71
	Butanol	+118	20/50	32.5	8.55
13	2-Propanol	+82	20/50	8.0	2.09
	2-Butanol	+100	20/50	18.8	4.95
14	*tert*-Butyl alcohol	+83	20/50	10.0	2.36
	tert-Amyl alcohol	+102	20/50	24.8	6.53
15	Acetaldehyde	+20	20/50	2.6	0.68
	Propionaldehyde	+50	20/50	5.4	1.42
	Butyraldehyde	+75	20/50	11.8	3.12
	Valeraldehyde	+103	20/50	26.4	6.95
16	Acetone	+56	20/50	5.7	1.50
	2-Butanone	+80	20/50	12.4	3.26
	2-Pentanone	+103	20/50	24.6	6.47
	2-Heptanone	+150	20/50	—	—
17	Methyl acetate	+58	20/50	6.4	1.67
	Ethyl acetate	+77	20/50	11.6	3.05
	n-Propyl acetate	+102	20/50	24.4	6.42
	n-Butyl acetate	+126	20/50	52.1	13.7
18	Diethyl ether	+35	20/50	4.2	1.12
	Diisopropyl ether	+68	20/50	8.8	2.30
	Di-*n*-butyl ether	+138	20/50	75.9	20.0
Misc.	Air	—	20/48	(1.50)	0.00
	Carbon monoxide	−190	20/48	0.00	0.00
	Carbon dioxide	−78	20/48	0.20	0.05
	Neopentane	+10	20/48	1.95	0.53
	Isooctane	+99	20/48	18.1	4.89
	Water	+100	20/48	7.0	1.84

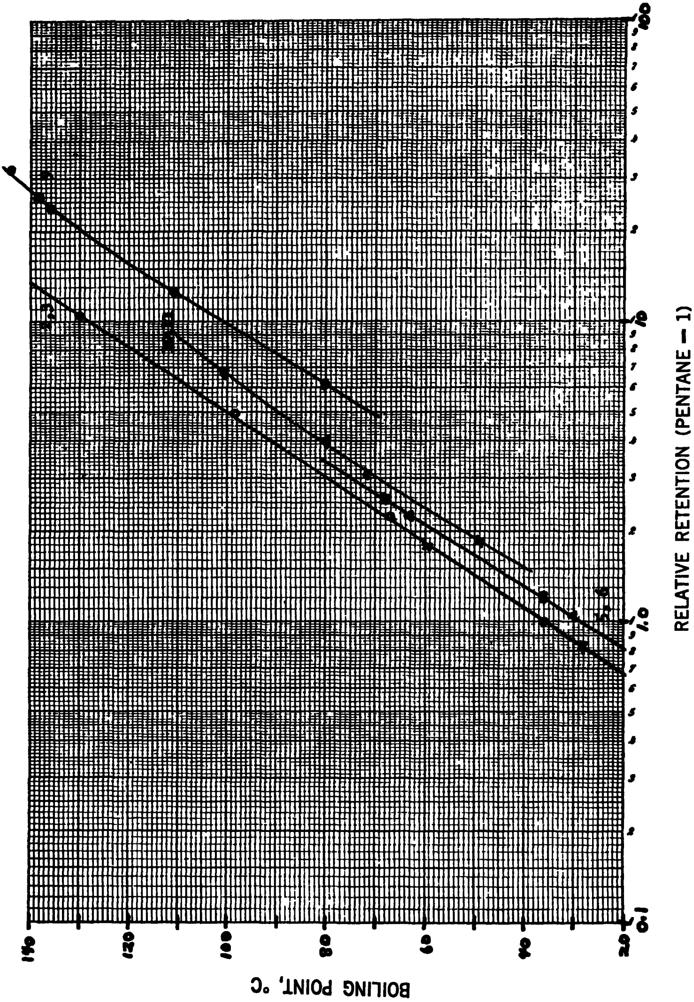

FIG 3 Separation of hydrocarbons on di-2-ethylhexyl sebacate (B) at 100°C.

RETENTION DATA, COLUMN C

Silicone oil (D. C. #200), 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature: 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	30/100	0.00	0.00
	Ethane	−89	30/100	0.30	0.05
	Propane	−42	30/100	0.90	0.14
	Butane	−0.5	30/100	2.30	0.35
2	Pentane	+36	30/100	6.50	1.00
	Hexane	+69	30/100	16.0	2.46
	Heptane	+98	30/100	38.7	5.95
	Octane	+126	30/100	92.6	14.25
3	2-Methylpropane	−12	30/100	1.90	0.29
	2-Methylbutane	+28	30/100	5.00	0.77
	2-Methylpentane	+60	30/100	12.4	1.91
4	Ethylene	−104	30/100	0.25	0.04
	Propylene	−48	30/100	0.90	0.14
	Isobutene	−6.9	30/100	2.35	0.36
	Butene-1	−6.3	30/100	2.35	0.36
	trans-Butene-2	+0.9	30/100	2.85	0.44
	cis-Butene-2	+3.7	30/100	3.25	0.50
5	Pentene-1	+30.0	30/100	5.80	0.89
	Hexene-1	+63.5	30/100	14.5	2.23
6	*trans*-Pentene-2	+36.3	30/100	6.90	1.06
	cis-Pentene-2	+36.9	30/100	7.40	1.14
	trans-Hexene-2	+67.9	30/100	16.5	2.54
	cis-Hexene-2	+68.8	30/100	18.2	2.80
7	Propadiene	−34	30/100	1.30	0.20
	Butadiene-1,3	−4	30/100	3.20	0.39
	2-Methylbutadiene-1,3	+34	30/100	6.65	1.02
8	Acetylene	−84	30/100	0.30	0.05
	Propyne	−23	30/100	1.50	0.23
	Butyne-1	+8	30/100	2.90	0.45
Misc.	Air	—	30/100	(1.05)	0.00
	Carbon monoxide	−190	30/100	0.00	0.00
	Carbon dioxide	−78	30/100	0.20	0.03
	Neopentane	+10	30/100	2.90	0.45
	Isooctane	+99	30/100	37.0	5.69

RETENTION DATA, COLUMN C—*Continued*

Silicone oil (D. C. #200), 20% by weight on 60–80 mesh Chromosorb, length: 4 meters; temperature: 100° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	30/82	0.00	0.00
	Ethane	−89	30/82	0.10	0.04
	Propane	−42	30/82	0.50	0.21
	Butane	−0.5	30/82	1.20	0.50
2	Pentane	+36	30/80	2.40	1.00
	Hexane	+69	30/80	4.90	2.04
	Heptane	+98	30/80	9.70	4.04
	Octane	+126	30/80	19.0	7.92
3	2-Methylpropane	−12	30/80	0.90	0.38
	2-Methylbutane	+28	30/80	2.00	0.83
	2-Methylpentane	+60	30/80	3.80	1.58
4	Ethylene	−104	30/80	0.15	0.06
	Propylene	−48	30/80	0.50	0.21
	Isobutene	−6.9	30/80	1.05	0.44
	Butene-1	−6.3	30/80	1.05	0.44
	trans-Butene-2	+0.9	30/80	1.20	0.50
	cis-Butene-2	+3.7	30/80	1.40	0.58
5	Pentene-1	+30.0	30/80	2.30	0.96
	Hexene-1	+63.5	30/80	4.40	1.83
6	*trans*-Pentene-2	+36.3	30/79	2.40	1.00
	cis-Pentene-2	+36.9	30/79	2.60	1.08
	trans-Hexene-2	+67.9	30/79	5.00	2.08
	cis-Hexene-2	+68.8	30/79	5.30	2.20
7	Propadiene	−34	30/81	0.80	0.33
	Butadiene-1,3	−4	30/81	1.40	0.48
	2-Methylbutadiene-1,3	+34	30/81	2.20	0.92
8	Acetylene	−84	30/82	0.20	0.08
	Propyne	−23	30/82	0.70	0.29
	Butyne-1	+8	30/82	1.30	0.54
9	Benzene	80	30/79	7.5	3.12
	Toluene	111	30/79	14.9	6.21
	Ethylbenzene	136	30/79	29.7	12.4
	p-Xylene	138.4	30/79	29.7	12.4
	m-Xylene	139.1	30/79	29.7	12.4
	o-Xylene	144.4	30/79	34.1	14.2
	Isopropylbenzene	152	30/79	44.2	18.4

RETENTION DATA, COLUMN C—*Continued*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
10	Cyclopentane	49	30/81	3.9	1.62
	Methylcyclopentane	72	30/81	6.1	2.54
11	Cyclohexane	81	30/81	7.9	3.29
	Methylcyclohexane	101	30/81	12.2	5.08
12	Methanol	65	30/72	2.0	0.83
	Ethanol	78	30/72	2.0	0.83
	Propanol	97	30/72	3.8	1.58
	Butanol	118	30/72	8.0	3.33
13	2-Propanol	82	30/82	3.0	1.25
	2-Butanol	100	30/82	5.8	2.42
14	*tert*-Butyl alcohol	83	30/82	3.2	1.33
	tert-Amyl alcohol	102	30/82	7.1	2.96
15	Acetaldehyde	20	30/72	1.3	0.54
	Propionaldehyde,	50	30/72	2.1	0.88
	Butyraldehyde	75	30/72	4.2	1.75
	Valeraldehyde	103	30/72	9.2	3.83
16	Acetone	56	30/72	2.6	1.08
	2-Butanone	80	30/72	4.8	2.00
	2-Pentanone	103	30/72	9.7	4.01
	2-Heptanone	150	30/72	32.7	13.6
17	Methyl acetate	58	30/82	3.7	1.54
	Ethyl acetate	77	30/82	6.0	2.50
	n-Propyl acetate	102	30/82	11.7	4.88
	n-Butyl acetate	126	30/82	23.0	9.58
18	Diethyl ether	35	30/82	2.4	1.00
	Diisopropyl ether	68	30/82	4.8	2.00
	Di-*n*-butyl ether	138	30/82	31.3	13.0
Misc	Air	—	30/82	(1.15)	0.00
	Carbon monoxide	−190	30/82	0.00	0.00
	Carbon dioxide	−78	30/82	0.20	0.08
	Neopentane	10	30/82	1.40	0.58
	Isooctane	99	30/82	9.60	4.00
	Water	100	30/82	5.2	2.17

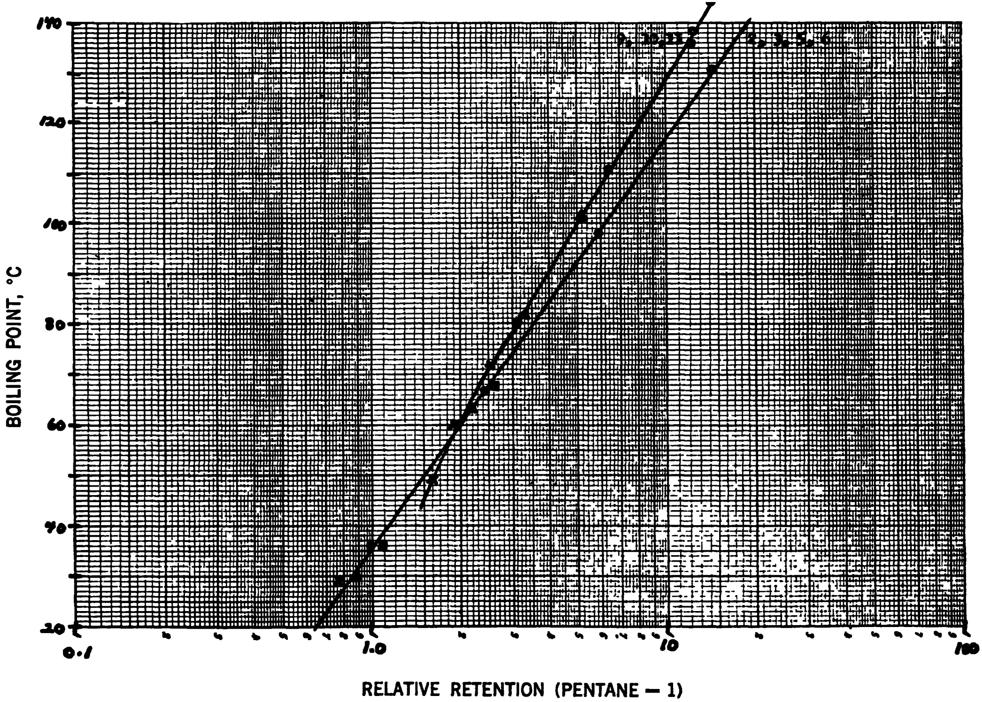

Fig 5. Separation of hydrocarbons on silicone oil (C) at 100° C.

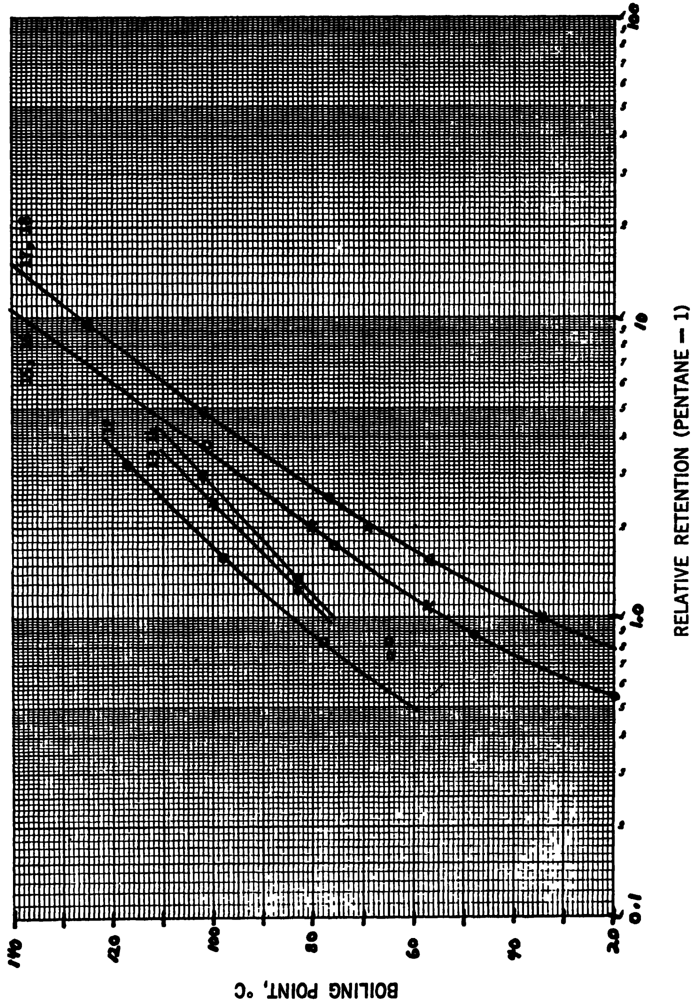

FIG. 6. Separation of oxygenated compounds on silicone oil (C) at 100° C

RETENTION DATA, COLUMN E

Dimethylsulfolane (2,4-dimethyltetrahydrothiophene-1,1-dioxide), 33% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature: 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	20/66	0.00	0.00
	Ethane	−89	20/66	0.20	0.04
	Propane	−42	20/66	0.65	0.14
	Butane	−0.5	20/66	1.85	0.40
2	Pentane	36	20/66	4.60	1.00
	Hexane	69	20/66	10.6	2.30
	Heptane	98	20/66	23.8	5.17
	Octane	126	20/66	54.7	11.9
3	2-Methylpropane	−12	20/66	1.30	0.28
	2-Methylbutane	+28	20/66	3.50	0.76
	2-Methylpentane	+60	20/66	7.95	1.73
4	Ethylene	−104	20/66	0.40	0.09
	Propylene	−48	20/66	1.20	0.26
	Isobutene	−6.9	20/66	3.05	0.66
	Butene-1	−6.3	20/66	3.05	0.66
	trans-Butene-2	+0.9	20/66	3.70	0.80
	cis-Butene-2	+3.7	20/66	4.25	0.92
5	Pentene-1	30.0	20/66	6.60	1.43
	Hexene-1	63.5	20/66	15.8	3.43
6	*trans*-Pentene-2	36 3	20/66	7.95	1.73
	cis-Pentene-2	36.9	20/66	8.70	1.89
	trans-Hexene-2	67.9	20/66	17.4	3.78
	cis-Hexene-2	68.8	20/66	19.7	4.28
7	Propadiene	−34	20/66	3.40	0.74
	Butadiene-1,3	−4	20/66	6.10	1.33
	2-Methylbutadiene-1,3	+34	20/66	15.3	3.33
8	Acetylene	−84	20/66	2.30	0.50
	Propyne	−23	20/66	6.50	1.41
	Butyne-1	+8	20/66	12.5	2.72
10	Cyclopentane	49	20/66	8.30	1.80
	Methylcyclopentane	72	20/66	12 0	2.61
11	Cyclohexane	81	20/66	25.5	5.54
	Methylcyclohexane	101	20/66	39.6	8.61
Misc.	Air	—	20/66	(1.10)	0.00
	Carbon monoxide	−190	20/66	0.00	0.00
	Carbon dioxide	−78	20/66	0.70	0.15
	2,2-Dimethylpropane	10	20/66	1.85	0 40
	2,2-Dimethylbutane	50	20/66	5.95	1.29
	2,3-Dimethylbutane	58	20/66	8.00	1.74
	3-Methylpentane	64	20/66	9.40	2.04
	Isooctane	99	20/66	20.7	4.50

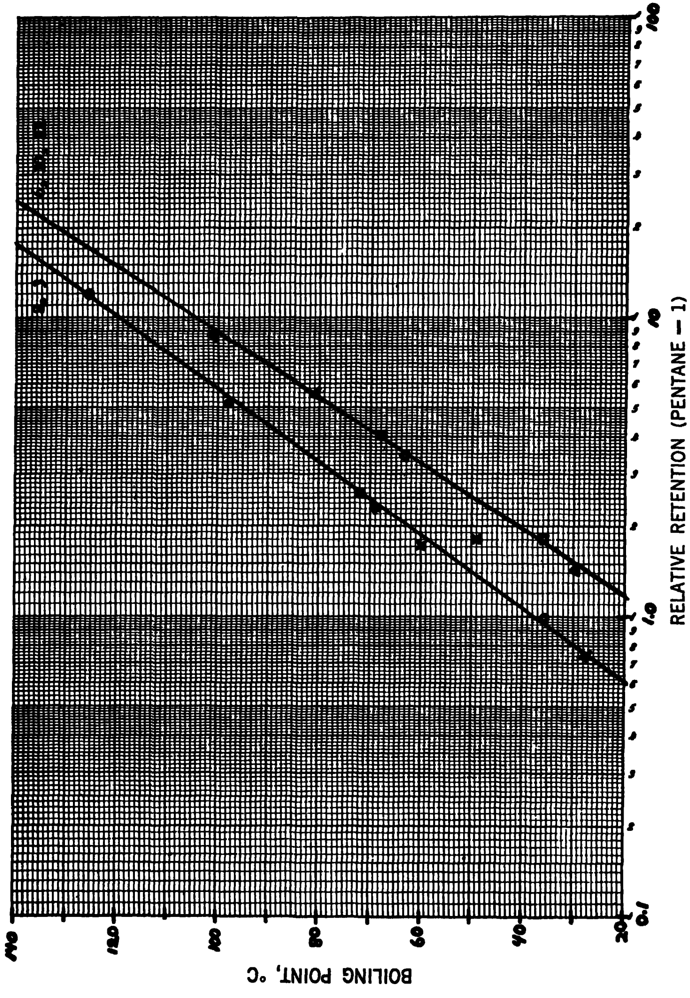

FIG 7 Separation of hydrocarbons on dimethylsulfolane (E) at 50° C

Retention Data, Column K

Polyethylene glycol (Carbowax 1500), 20% by weight on 60–80 mesh Chromosorb; length. 4 meters; temperature: 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
1	Methane	−162	15/48	0 00	0 00
	Ethane	−89	15/48	0 10	0 07
	Propane	−42	15/48	0 30	0 21
	Butane	−0 5	15/48	0 70	0 48
2	Pentane	+36	15/48	1 45	1 00
	Hexane	+69	15/48	3 10	2 14
	Heptane	+98	15/48	6 90	4 76
	Octane	+126	15/48	15 3	10 6
3	2-Methylpropane	−12	15/48	0 60	0 41
	2-Methylbutane	+28	15/48	1 00	0 69
	2-Methylpentane	+60	15/48	2 20	1 52
4	Ethylene	−104	15/48	0 10	0 07
	Propylene	−48	15/48	0 30	0 21
	Isobutene	−6 9	15/48	0 90	0 62
	Butene-1	−6 3	15/48	0 90	0 62
	trans-Butene-2	+0 9	15/48	1 10	0 76
	cis-Butene-2	+3 7	15/48	1 40	0 97
5	Pentene-1	+30 0	15/48	1 90	1 31
	Hexene-1	+63 5	15/48	4 40	3 03
6	*trans*-Pentene-2	+36 3	15/48	2 40	1 66
	cis-Pentene 2	+36 9	15/48	2 65	1 83
	trans-Hexene-2	+67 9	15/48	4 95	3 41
	cis-Hexene-2	+68 8	15/48	5 80	4 00
7	Propadiene	−34	15/48	1 30	0 90
	Butadiene-1,3	−4	15/48	1 90	1 31
	2-Methylbutadiene-1,3	+34	15/48	4 20	2 90
8	Acetylene	−84	15/48	1 10	0 76
	Propyne	−23	15/48	2 50	1 72
	Butyne-1	+8	15/48	4 30	2 97
Misc	Air	--	15/48	(1 60)	0 00
	Carbon monoxide	−190	15/48	0 00	0 00
	Carbon dioxide	−78	15/48	0 25	0 17
	Neopentane	+10	15/48	0 50	0 34
	Isooctane	+99	15/48	5 80	4 00

RETENTION DATA, COLUMN K—*Continued*

Polyethylene glycol (Carbowax 1500), 20% by weight on 60–80 mesh Chromosorb length: 4 meters; temperature: 100° C.

Mix no.	Component	Boiling point, °C	*P/F*	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	25/78	0.00	0.00
	Ethane	−89	25/78	0.00	0.00
	Propane	−42	25/78	0.10	0.25
	Butane	−0.5	25/78	0.20	0.50
2	Pentane	+36	25/76	0.40	1.00
	Hexane	+69	25/76	0.80	2.00
	Heptane	+98	25/76	1.45	3.62
	Octane	+126	25/76	2.70	6.75
3	2-Methylpropane	−12	25/76	0.25	0.63
	2-Methylbutane	+28	25/76	0.30	0.75
	2-Methylpentane	+60	25/76	0.60	1.50
4	Ethylene	−104	25/76	0.05	0.12
	Propylene	−48	25/76	0.20	0.50
	Isobutene	−6.9	25/76	0.30	0.75
	Butene-1	−6.3	25/76	0.30	0.75
	trans-Butene-2	+0.9	25/76	0.35	0.88
	cis-Butene-2	+3.7	25/76	0.40	1.00
5	Pentene-1	+30.0	25/76	0.60	1.50
	Hexene-1	+63.5	25/76	1.00	2.50
6	*trans*-Pentene-2	+36.3	25/76	0.60	1.50
	cis-Pentene-2	+36.9	25/76	0.70	1.75
	trans-Hexene-2	+67.9	25/76	1.20	3.00
	cis-Hexene-2	+68.8	25/76	1.30	3.25
7	Propadiene	−34	25/76	0.45	1.13
	Butadiene-1,3	−4	25/76	0.55	1.38
	2-Methylbutadiene-1,3	+34	25/76	1.00	2.50
8	Acetylene	−84	25/76	0.30	0.75
	Propyne	−23	25/76	0.70	1.75
	Butyne-1	+8	25/76	1.10	2.75
9	Benzene	+80	25/78	7.6	19.0
	Toluene	+111	25/78	13.2	33.0
	Ethylbenzene	+136	25/78	21.2	53.0
	p-Xylene	+138.4	25/78	23.3	58.2
	m-Xylene	+139.1	25/78	23.3	58.2
	o-Xylene	+144.4	25/78	30.1	75.2
	Isopropylbenzene	+152	25/78	28.2	70.5

Retention Data, Column K—*Continued*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio ($nC_5 = 1$)
10	Cyclopentane	+49	25/78	1.00	2.50
	Methylcyclopentane	+72	25/78	1.30	3.25
11	Cyclohexane	+81	25/78	1.95	4.88
	Methylcyclohexane	+101	25/78	2 65	6.64
12	Methanol	+65	25/78	7.6	19.0
	Ethanol	+78	25/78	9.0	22.5
	Propanol	+97	25/78	16 2	40.5
	Butanol	+118	25/78	29.8	74.5
13	2-Propanol	+82	25/78	8.3	20.8
	2-Butanol	+100	25/78	14 6	36.5
14	*tert*-Butyl alcohol	+83	25/78	6.9	17.2
	tert-Amyl alcohol	+102	25/78	13 4	33.5
15	Acetaldehyde	+20	25/78	2.0	5.00
	Propionaldehyde	+50	25/78	3.4	8 50
	Butyraldehyde	+75	25/78	5.8	14.5
	Valderaldehyde	+103	25/78	10 7	26 8
16	Acetone	+56	25/78	4.2	10 5
	2-Butanone	+80	25/78	6.9	17.2
	2-Pentanone	+103	25/78	10 8	27.0
	2-Heptanone	+150	25/78	33 7	84 3
17	Methyl acetate	+58	25/78	3.9	9 75
	Ethyl acetate	+77	25/78	5.6	14.0
	n-Propyl acetate	+102	25/78	9.4	23 5
	n-Butyl acetate	+126	25/78	16.4	41 0
18	Diethyl ether	+35	25/78	1.0	2.50
	Diisopropyl ether	+68	25/78	1.3	3.25
	Di-*n*-butyl ether	+138	25/78	8 2	20.5
Misc.	Air	—	25/78	(1.10)	0.00
	Carbon monoxide	−190	25/78	0.00	0.00
	Carbon dioxide	−78	25/78	0.10	0.25
	Neopentane	+10	25/78	0.20	0.50
	Isooctane	+99	25/78	1.20	3.00
	Water	+100	25/78	24.3	60.8

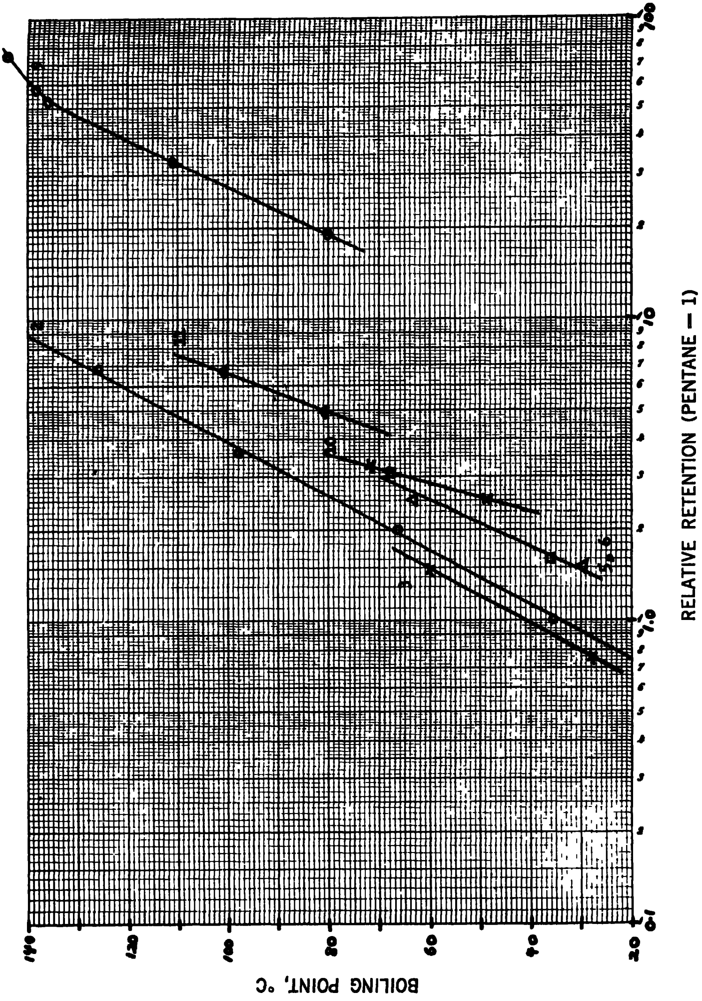

Fig 8 Separation of hydrocarbons on polyethylene glycol (K) at 100° C

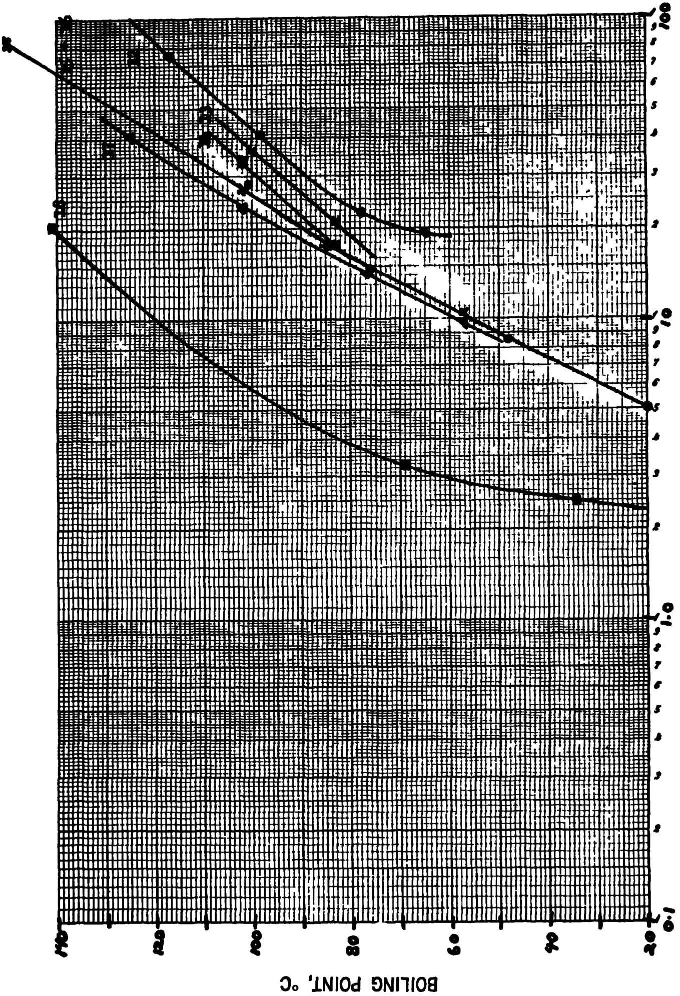

FIG. 9. Separation of oxygenated compounds on polyethylene glycol (K) at 100° C

RETENTION DATA, COLUMN O

Silicone grease (D. C. high-vacuum grease), 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature: 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	10/46	0.10	0.02
	Ethane	−89	10/46	0.40	0.06
	Propane	−42	10/46	1.00	0.15
	Butane	−0.5	10/46	2.70	0.41
2	Pentane	+36	10/46	6.65	1.00
	Hexane	+69	10/46	6.30	2.45
	Heptane	+98	10/46	39.8	5.98
	Octane	+126	10/46	98.3	14.8
3	2-Methylpropane	−12	10/46	1.90	0.29
	2-Methylbutane	+28	10/46	5.10	0.77
	2-Methylpentane	+60	10/46	12.3	1.85
4	Ethylene	−104	10/46	0.20	0.03
	Propylene	−48	10/46	0.85	0.13
	Isobutene	−6.9	10/46	2.40	0.36
	Butene-1	−6.3	10/46	2.40	0.36
	trans-Butene-2	+0.9	10/46	2.90	0.44
	cis-Butene-2	+3.7	10/46	3.35	0.50
5	Pentene-1	+30.0	10/46	5.80	0.87
	Hexene-1	+63.5	10/46	14.7	2.21
6	*trans*-Pentene-2	+36.3	10/46	7.05	1.06
	cis-Pentene-2	+36.9	10/46	7.60	1.14
	trans-Hexene-2	+67.9	10/46	16.9	2.54
	cis-Hexene-2	+68.8	10/46	18.6	2.79
7	Propadiene	−34	10/46	1.35	0.20
	Butadiene-1,3	−4	10/46	2.50	0.38
	2-Methylbutadiene-1,3	+34	10/46	6.70	1.01
8	Acetylene	−84	10/46	0.25	0.04
	Propyne	−23	10/46	1.35	0.20
	Butyne-1	+8	10/46	2.00	0.30
Misc.	Air	—	10/44	(1.50)	0.00
	Carbon monoxide	−190	10/46	0.00	0.00
	Carbon dioxide	−78	10/46	0.20	0.03
	Neopentane	+10	10/46	4.50	0.68
	Isooctane	+99	10/46	37.4	5.62

RETENTION DATA, COLUMN O—*Continued*

Silicone grease (D. C. high-vacuum grease), 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature. 100° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	14/55	0.10	0.06
	Ethane	−89	14/55	0.25	0.14
	Propane	−42	14/55	0.45	0.25
	Butane	−0.5	14/55	0.95	0.53
2	Pentane	+36	14/55	1.80	1.00
	Hexane	+69	14/55	3.50	1.94
	Heptane	+98	14/55	6.95	3.86
	Octane	+126	14/55	13.7	7.61
3	2-Methylpropane	−12	14/55	0.70	0.39
	2-Methylbutane	+28	14/55	1.20	0.67
	2-Methylpentane	+60	14/55	2.70	1.50
4	Ethylene	−104	14/55	0.15	0.08
	Propylene	−48	14/55	0.40	0.22
	Isobutene	−6.9	14/55	0.80	0.44
	Butene-1	−6.3	14/55	0.80	0.44
	trans-Butene-2	+0.9	14/55	0.95	0.53
	cis-Butene-2	+3.7	14/55	1.00	0.56
5	Pentene-1	+30.0	14/55	1.40	0.78
	Hexene-1	+63.5	14/55	2.95	1.64
6	*trans*-Pentene-2	+36.3	14/55	1.85	1.03
	cis-Pentene-2	+36.9	14/55	2.00	1.11
	trans-Hexene-2	+67.9	14/55	3.60	2.00
	cis-Hexene-2	+68.8	14/55	3.90	2.17
7	Propadiene	−34	14/55	0.55	0.31
	Butadiene-1,3	−4	14/55	0.90	0.50
	2-Methylbutadiene-1,3	+34	14/55	2.00	1.11
8	Acetylene	−84	14/55	0.15	0.08
	Propyne	−23	14/55	0.55	0.31
	Butyne-1	+8	14/55	0.95	0.53
9	Benzene	+80	20/91	3.75	3.26
	Toluene	+111	20/91	7.50	6.52
	Ethylbenzene	+136	20/91	13.8	12.0
	p-Xylene	+138.4	20/91	15.0	13.0
	m-Xylene	+139.1	20/91	15.0	13.0
	o-Xylene	+144.4	20/91	17.3	14.0
	Isopropylbenzene	+152	20/91	21.2	18.4

RETENTION DATA, COLUMN O—*Continued*

Mix no.	Component	Boiling point, °C	*P/F*	T_r, min (air = 0)	Ratio ($nC_5 = 1$)
10	Cyclopentane	+49	14/55	2.85	1.64
	Methylcyclopentane	+72	14/55	4.50	2.50
11	Cyclohexane	+81	14/55	5.75	3.19
	Methylcyclohexane	+101	14/55	8.65	4.80
12	Methanol	+65	14/55	2.0	1.11
	Ethanol	+78	14/55	2.0	1.11
	Propanol	+97	14/55	3.6	2.00
	Butanol	+118	14/55	8.4	4.66
13	2-Propanol	+82	14/55	2.0	1.11
	2-Butanol	+100	14/55	4.5	2.50
14	*tert*-Butyl alcohol	+83	14/55	2.3	1.28
	tert-Amyl alcohol	+102	14/55	5.0	2.78
15	Acetaldehyde	+20	14/55	0.8	0.44
	Propionaldehyde	+50	14/55	1.6	0.89
	Butyraldehyde	+75	14/55	3.4	1.90
	Valderaldehyde	+103	14/55	7.6	4.22
16	Acetone	+56	14/55	2.0	1.11
	2-Butanone	+80	14/55	3.8	2.11
	2-Pentanone	+103	14/55	7.0	3.89
	2-Heptanone	+150	14/55	25.7	14.3
17	Methyl acetate	+58	14/55	2.2	1.22
	Ethyl acetate	+77	14/55	4.0	2.22
	n-Propyl acetate	+102	14/55	7.8	4.33
	n-Butyl acetate	+126	14/55	15.0	8.33
18	Diethyl ether	+35	14/55	1.9	1.05
	Diisopropyl ether	+68	14/55	3.5	1.94
	Di-*n*-butyl ether	+138	14/55	23.0	12.8
Misc	Air	—	14/55	(1.20)	0.00
	Carbon monoxide	−190	14/55	0.00	0.00
	Carbon dioxide	−78	14/55	0.10	0.06
	Neopentane	+10	14/55	1.80	1.00
	Isooctane	+99	14/55	6.80	3.78
	Water	+100	14/55	3.50	1.94

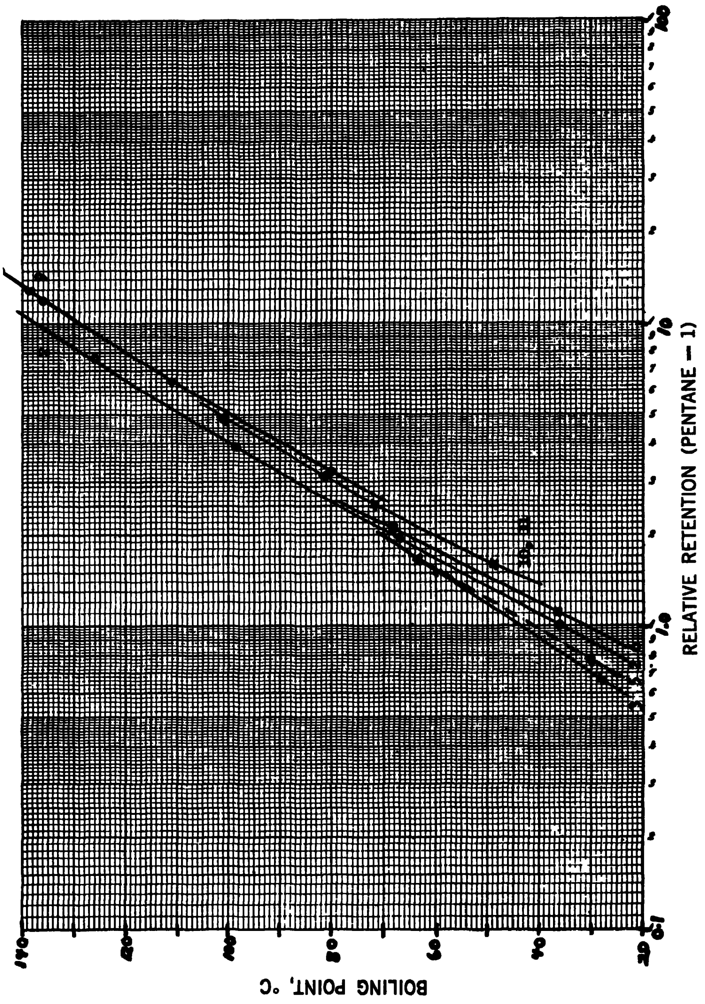

FIG 10 Separation of hydrocarbons on silicone grease (0) at 100° C.

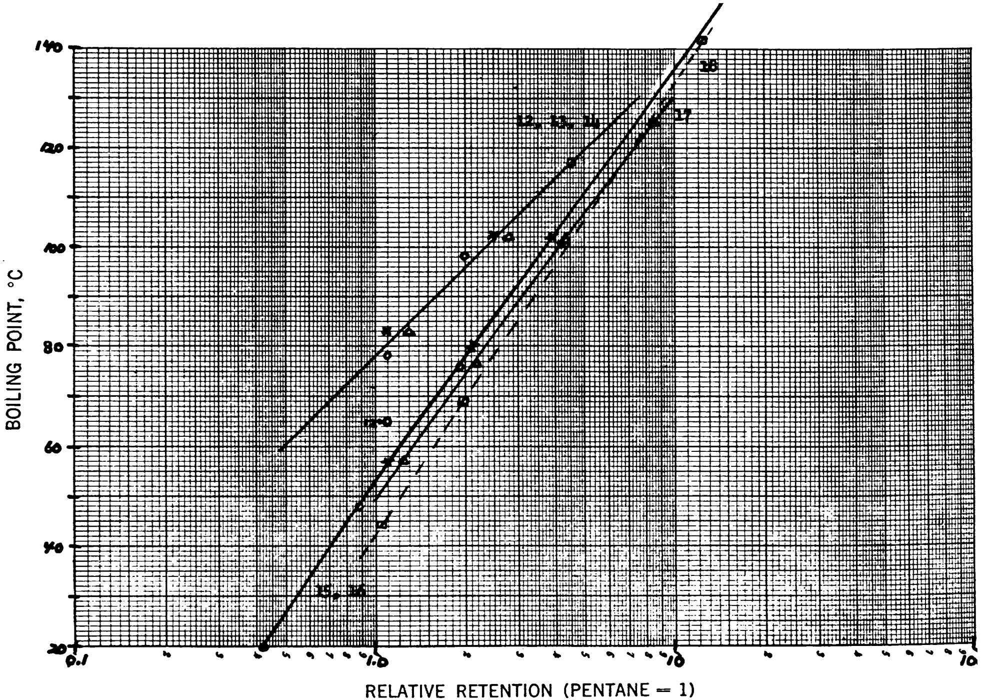

Fig. 11. Separation of oxygenated compounds on silicone grease (0) at 100° C.

RETENTION DATA, COLUMN P

Polydiethylene glycol succinate, 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature· 50° C.

Mix no	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
1	Methane	−162	20/66	0 00	0.00
	Ethane	−89	20/66	0 00	0 00
	Propane	−42	20/66	0 07	0 16
	Butane	−0 5	20/66	0 20	0.44
2	Pentane	+36	20/66	0 45	1 00
	Hexane	+69	20/66	0 85	1 89
	Heptane	+98	20/66	1 80	4 00
	Octane	+126	20/66	4 15	9 22
3	2-Methylpropane	−12	20/66	0.20	0 44
	2-Methylbutane	+28	20/66	0 30	0 67
	2-Methylpentane	+60	20/66	0 65	1 44
4	Ethylene	−104	20/66	0 05	0 11
	Propylene	−48	20/66	0 20	0.44
	Isobutene	−6 9	20/66	0 35	0 78
	Butene-1	−6 3	20/66	0 35	0 78
	trans-Butene-2	+0 9	20/66	0 50	1 11
	cis-Butene-2	+3 7	20/66	0 50	1 11
5	Pentene-1	+30.0	20/66	0 60	1 33
	Hexene-1	+63 5	20/66	1.25	2.78
6	*trans*-Pentene-2	+36 3	20/66	0 95	2 11
	cis-Pentene-2	+36 9	20/66	0.95	2 11
	trans-Hexene-2	+67 9	20/66	1.60	3.56
	cis-Hexene-2	+68.8	20/66	1 60	3 56
7	Propadiene	−34	20/66	0 50	1.11
	Butadiene-1,3	−4	20/66	0 75	1 67
	2-Methylbutadiene-1,3	+34	20/66	1.35	3.00
8	Acetylene	−84	20/66	0 35	0 78
	Propyne	−23	20/66	1 00	2 22
	Butyne-1	+8	20/66	1 50	3 33
Misc.	Air	—	20/66	(1 15)	0 00
	Carbon monoxide	−190	20/66	0.00	0 00
	Carbon dioxide	−78	20/66	0 20	0 44
	Neopentane	+10	20/66	0.20	0 44
	Isooctane	+99	20/66	1 80	4 00

RETENTION DATA, COLUMN P—*Continued*

Polydiethylene glycol succinate, 20% by weight on 60–80 mesh Chromosorb; length. 4 meters, temperature: 100° C.

Mix no	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	20/52	0.00	0.00
	Ethane	−89	20/52	0.00	0.00
	Propane	−42	20/52	0.00	0.00
	Butane	−0.5	20/52	0.10	0.40
2	Pentane	+36	20/52	0.25	1.00
	Hexane	+69	20/52	0.45	1.80
	Heptane	+98	20/52	0.70	2.80
	Octane	+126	20/52	1.10	4.40
3	2-Methylpropane	−12	20/52	0.10	0.40
	2-Methylbutane	+28	20/52	0.15	0.60
	2-Methylpentane	+60	20/52	0.25	1.00
4	Ethylene	−104	20/52	0.00	0.00
	Propylene	−48	20/52	0.10	0.40
	Isobutene	−6.9	20/52	0.15	0.60
	Butene-1	−6.3	20/52	0.15	0.60
	trans-Butene-2	+0.9	20/52	0.20	0.80
	cis-Butene-2	+3.7	20/52	0.20	0.80
5	Pentene-1	+30.0	20/52	0.25	1.00
	Hexene-1	+63.5	20/52	0.45	1.80
6	*trans*-Pentene-2	+36.3	20/52	0.30	1.20
	cis-Pentene-2	+36.9	20/52	0.30	1.20
	trans-Hexene-2	+67.9	20/52	0.60	2.40
	cis-Hexene-2	+68.8	20/52	0.60	2.40
7	Propadiene	−34	20/52	0.30	1.20
	Butadiene-1,3	−4	20/52	0.40	1.60
	2-Methylbutadiene-1,3	+34	20/52	0.60	2.40
8	Acetylene	−84	20/52	0.20	0.80
	Propyne	−23	20/52	0.50	2.00
	Butyne-1	+8	20/52	0.60	2.40
9	Benzene	+80	20/52	4.60	18.4
	Toluene	+110	20/52	7.60	30.4
	Ethylbenzene	+136	20/52	11.2	44.8
	p-Xylene	+138.4	20/52	12.2	48.8
	m-Xylene	+139.1	20/52	12.8	51.2
	o-Xylene	+144.4	20/52	16.3	65.2
	Isopropylbenzene	+152	20/52	13.9	55.6

RETENTION DATA, COLUMN P—*Continued*

Mix no.	Component	Boiling point, °C	*P/F*	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
10	Cyclopentane	+49	20/52	0.40	1.60
	Methylcyclopentane	+72	20/52	0.55	2.20
11	Cyclohexane	+81	20/52	0.80	3.20
	Methylcyclohexane	+101	20/52	1.00	4.00
12	Methanol	+65	20/52	7.00	28.0
	Ethanol	+78	20/52	7.90	31.6
	Propanol	+97	20/52	12.4	49.6
	Butanol	+118	20/52	20.6	82.4
13	2-Propanol	+82	20/52	7.50	30.0
	2-Butanol	+100	20/52	11.7	46.8
14	*tert*-Butyl alcohol	+83	20/52	6.60	26.4
	tert-Amyl alcohol	+102	20/52	11.4	45.6
15	Acetaldehyde	+20	20/52	1.85	7.40
	Propionaldehyde	+50	20/52	3.05	12.2
	Butyraldehyde	+75	20/52	4.70	18.8
	Valeraldehyde	+103	20/52	7.80	31.2
16	Acetone	+56	20/52	4.80	19.2
	2-Butanone	+80	20/52	6.90	27.6
	2-Pentanone	+103	20/52	9.60	38.4
	2-Heptanone	+150	20/52	24.8	99.2
17	Methyl acetate	+58	20/52	4.00	16.0
	Ethyl acetate	+77	20/52	5.05	20.2
	n-Propyl acetate	+102	20/52	7.60	30.4
	n-Butyl acetate	+126	20/52	12.2	48.8
18	Diethyl ether	+35	20/52	0.80	3.20
	Diisopropyl ether	+68	20/52	3.35	13.4
	Di-*n*-butyl ether	+138	20/52		
Misc.	Air	—	20/52	(1.20)	0.00
	Carbon monoxide	−190	20/52	0.00	0.00
	Carbon dioxide	−78	20/52	0.10	0.40
	Neopentane	+10	20/52	0.10	0.40
	Isooctane	+99	20/52	0.75	3.00
	Water	+100	20/52	20.0	80.0

RETENTION DATA, COLUMN P—*Continued*

Polydiethylene glycol succinate, 20% by weight on 60–80 mesh Chromosorb; length: 2 meters; temperature: 210° C; inlet pressure: 20 psig.

Fatty acid methyl ester	T_r, min (air = 0)	Ratio (palmitate = 1)
Air	(0.40)	0.00
Caprylate (C_8)	0.55	0.12
Caprate (C_{10})	0.80	0.17
Laurate	1 60	0.35
Myristate	2.75	0.60
Palmitate	4.60	1.00
Palmitoleate	5.30	1.15
Stearate	8.00	1.74
Oleate	9.20	2.00
Linoleate	11.2	2.44
Linolenate	13 7	2.98
Arachidate (C_{20})	12.9	2.80

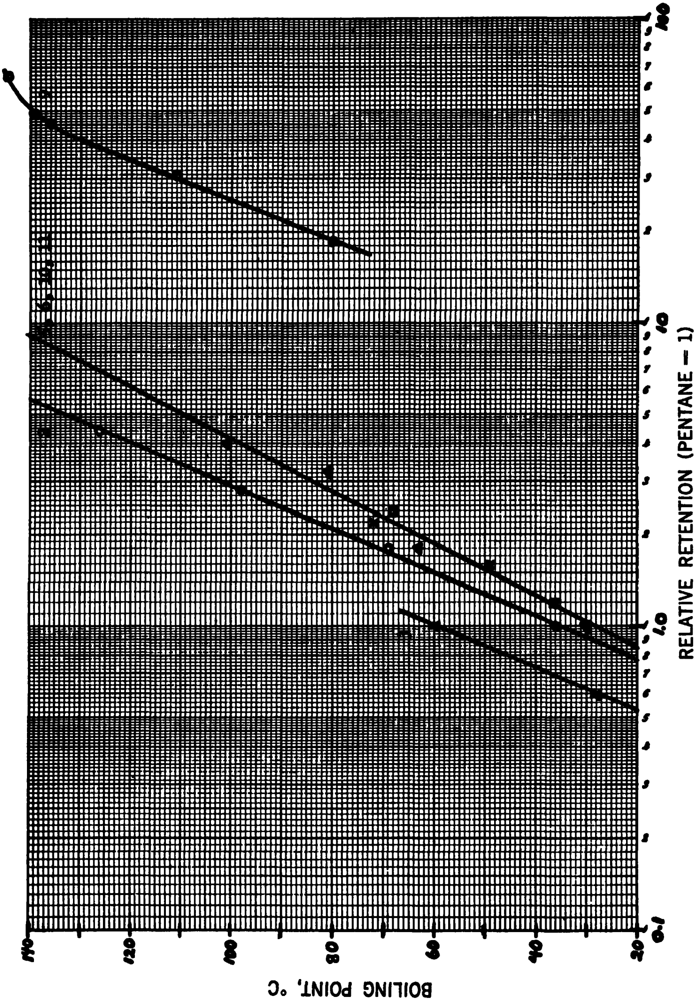

Fig. 12. Separation of hydrocarbons on polydiethylene glycol succinate (P) at 100° C.

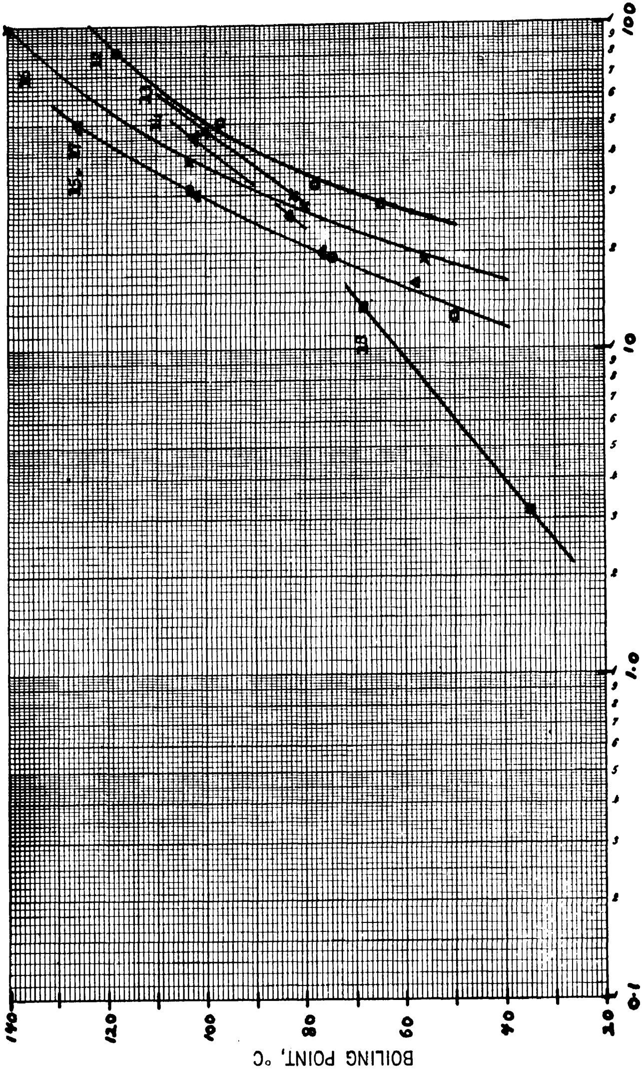

FIG. 13. Separation of oxygenated compounds on polydiethylene glycol succinate (P) at 100° C.

RETENTION DATA, COLUMN Q

Apiezon L grease, 20% by weight on 60–80 mesh Chromosorb; length 4 meters; temperature · 50° C

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	15/56	0.10	0.01
	Ethane	−89	15/56	0.35	0.05
	Propane	−42	15/56	0.90	0.12
	Butane	−0.5	15/56	2.80	0.37
2	Pentane	+36	15/56	7.60	1.00
	Hexane	+69	15/56	20.2	2.66
	Heptane	+98	15/56	54.7	7.20
	Octane	+126	15/56	—	—
3	2-Methylpropane	−12	15/56	1.80	0.24
	2-Methylbutane	+28	15/56	5.60	0.74
	2-Methylpentane	+60	15/56	14.8	1.95
4	Ethylene	−104	15/56	0.25	0.03
	Propylene	−48	15/56	0.85	0.11
	Isobutene	−6.9	15/56	2.35	0.31
	Butene-1	−6.3	15/56	2.35	0.31
	trans-Butene-2	+0.9	15/56	3.05	0.40
	cis-Butene-2	+3.7	15/56	3.40	0.45
5	Pentene-1	+30.0	15/56	6.40	0.84
	Hexene-1	+63.5	15/56	17.6	2.32
6	*trans*-Pentene-2	+36.3	15/56	8.00	1.05
	cis-Pentene-2	+36.9	15/56	8.20	1.08
	trans-Hexene-2	+67.9	15/56	20.2	2.66
	cis-Hexene-2	+68.8	15/56	21.9	2.88
7	Propadiene	−34	15/56	1.30	0.17
	Butadiene-1,3	−4	15/56	2.60	0.34
	2-Methylbutadiene-1,3	+34	15/56	7.90	1.04
8	Acetylene	−84	15/56	0.20	0.03
	Propyne	−23	15/56	1.20	0.16
	Butyne-1	+8	15/56	2.60	0.34
Misc.	Air	—	15/56	(1.30)	0.00
	Carbon monoxide	−190	15/56	0.00	0.00
	Carbon dioxide	−78	15/56	0.20	0.03
	Neopentane	+10	15/56	2.75	0.36
	Isooctane	+99	15/56	47.7	6.27

RETENTION DATA, COLUMN Q—*Continued*

Apiezon L grease, 20% by weight on 60–80 mesh Chromosorb, length: 4 meters; temperature: 100° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
1	Methane	−162	15/46	0.00	0.00
	Ethane	−89	15/46	0.20	0.07
	Propane	−42	15/46	0.50	0.17
	Butane	−0.5	15/46	1.35	0.46
2	Pentane	+36	15/46	2.95	1.00
	Hexane	+69	15/46	6.35	2.15
	Heptane	+98	15/46	13.7	4.64
	Octane	+126	15/46	29.4	9.67
3	2-Methylpropane	−12	15/46	0.95	0.32
	2-Methylbutane	+28	15/46	2.35	0.80
	2-Methylpentane	+60	15/46	4.95	1.68
4	Ethylene	−194	15/46	0.20	0.07
	Propylene	−48	15/46	0.55	0.19
	Isobutene	−6.9	15/46	1.20	0.41
	Butene-1	−6.3	15/46	1.20	0.41
	trans-Butene-2	+0.9	15/46	1.45	0.49
	cis-Butene-2	+3.7	15/46	1.60	0.54
5	Pentene-1	+30.0	15/46	2.50	0.85
	Hexene-1	+63.5	15/46	5.55	1.88
6	*trans*-Pentene-2	+36.3	15/46	3.00	1.02
	cis-Pentene-2	+36.9	15/46	3.10	1.05
	trans-Hexene-2	+67.9	15/46	6.35	2.15
	cis-Hexene-2	+68.8	15/46	6.70	2.27
7	Propadiene	−34	15/46	0.80	0.27
	Butadiene-1,3	−4	15/46	1.35	0.46
	2-Methylbutadiene-1,3	+34	15/46	3.10	1.05
8	Acetylene	−84	15/46	0.15	0.05
	Propyne	−23	15/46	0.90	0.31
	Butyne-1	+8	15/46	1.35	0.46
9	Benzene	+80	25/94	7.3	4.42
	Toluene	+111	25/94	16.5	10.0
	Ethylbenzene	+136	25/94	32.0	19.4
	p-Xylene	+138.4	25/94	37.0	22.4
	m-Xylene	+139.1	25/94	37.0	22.4
	o-Xylene	+144.4	25/94	43.9	27.6
	Isopropylbenzene	+152	25/94	49.1	29.8

RETENTION DATA, COLUMN Q—*Continued*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC$_5$ = 1)
10	Cyclopentane	+49	15/46	5.55	1.88
	Methylcyclopentane	+72	15/46	8.80	2.98
11	Cyclohexane	+81	15/46	12.5	4.24
	Methylcyclohexane	+101	15/46	20.3	6.88
12	Methanol	+65	15/50	2.2	0.79
	Ethanol	+78	15/50	3.7	1.32
	Propanol	+97	15/50	4.9	1.75
	Butanol	+118	15/50	12.8	4.57
13	2-Propanol	+82	15/50	2.5	0.89
	2-Butanol	+100	15/50	7.0	2.50
14	*tert*-Butyl alcohol	+83	15/50	3.2	1.14
	tert-Amyl alcohol	+102	15/50	5.5	1.96
15	Acetaldehyde	+20	15/50	0.70	0.25
	Propionaldehyde	+50	15/50	2.4	0.86
	Butyraldehyde	+75	15/50	5.7	2.03
	Valeraldehyde	+103	15/50	14.2	5.62
16	Acetone	+56	15/50	2.4	0.86
	2-Butanone	+80	15/50	6.3	2.25
	2-Pentanone	+103	15/50	12.6	4.50
	2-Heptanone	+150	15/50	31.6	11.3
17	Methyl acetate	+58	15/50	3.0	1.07
	Ethyl acetate	+77	15/50	5.6	2.00
	n-Propyl acetate	+102	15/50	11.3	4.04
	n-Butyl acetate	+126	15/50	24.4	0.87
18	Diethyl ether	+35	15/50	2.6	0.93
	Diisopropyl ether	+68	15/50	4.9	1.75
	Di-*n*-butyl ether	+138	15/50	44.4	15.8
Misc	Air	—	15/46	(1.40)	0.00
	Carbon monoxide	−190	15/46	0.00	0.00
	Carbon dioxide	−78	15/46	0.15	0.05
	Neopentane	+10	15/46	1.30	0.44
	Isooctane	+99	15/46	12.6	4.28
	Water	+100	15/46	8.2	2.8

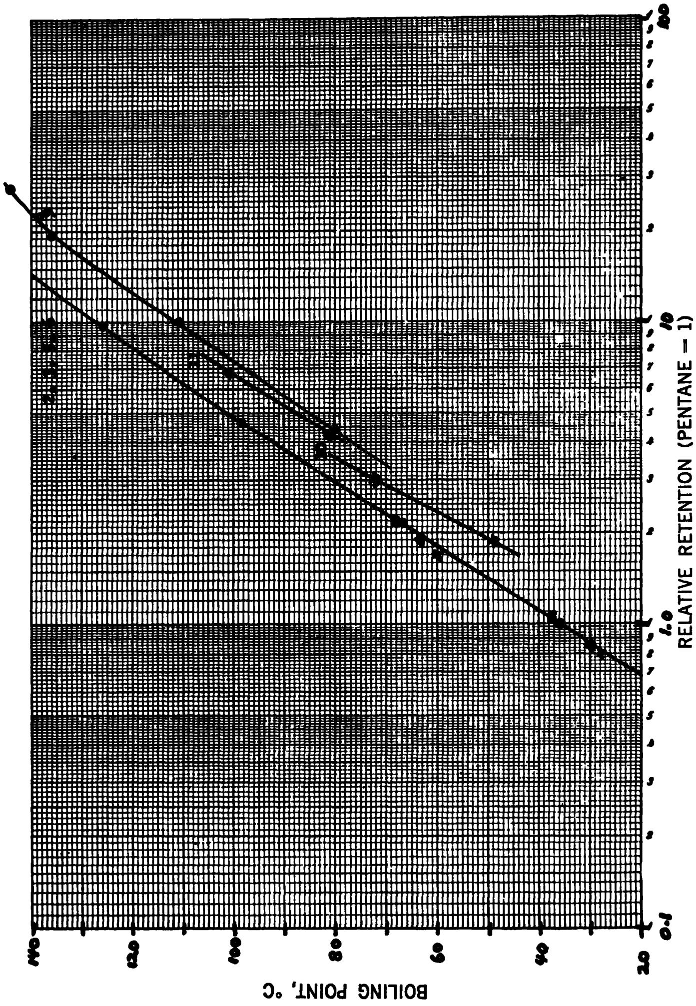

Fig. 14. Separation of hydrocarbons on Apiezon L (Q) at 100° C

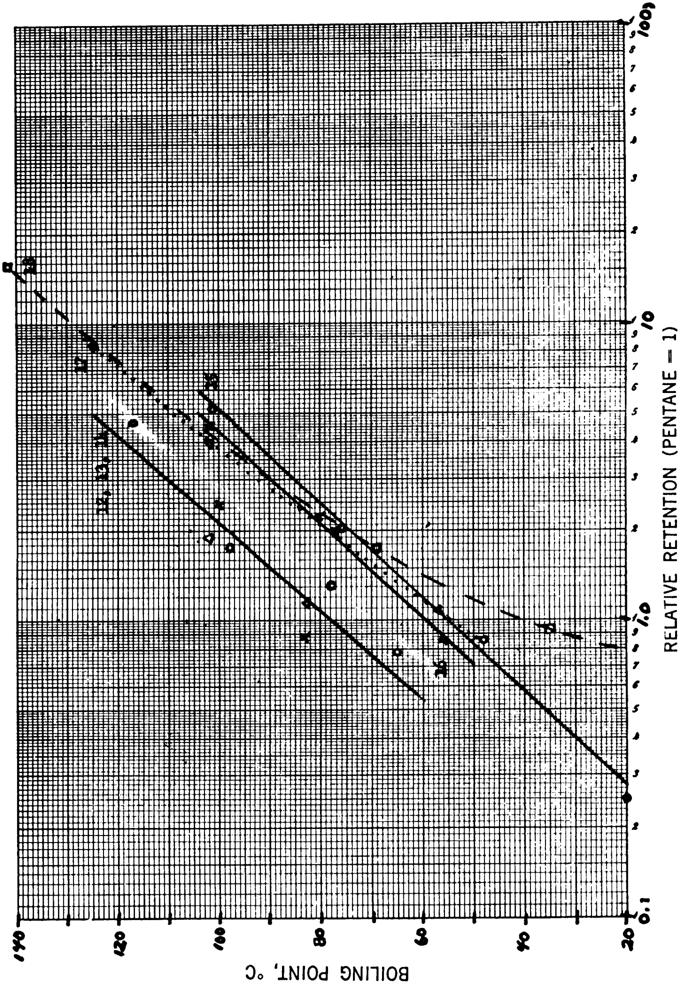

FIG. 15. Separation of oxygenated compounds on Apiezon L (Q) at 100° C.

RETENTION DATA, COLUMN R

Polypropylene glycol (UCON LB-550-X), 20% by weight on 60–80 mesh Chromosorb; length: 4 meters; temperature. 50° C.

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	20/60	0.10	0.02
	Ethane	−89	20/60	0.30	0.05
	Propane	−42	20/60	0.90	0.14
	Butane	−0.5	20/60	2.50	0.39
2	Pentane	+36	20/60	6.40	1.00
	Hexane	+69	20/60	16.7	2.61
	Heptane	+98	20/60	41.9	6.55
	Octane	+126	20/60	—	—
3	2-Methylpropane	−12	20/60	1.75	0.27
	2-Methylbutane	+28	20/60	5.00	0.78
	2-Methylpentane	+60	20/60	12.6	1.97
4	Ethylene	−104	20/60	0.30	0.05
	Propylene	−48	20/60	1.05	0.16
	Isobutene	−6.9	20/60	2.80	0.44
	Butene-1	−6.3	20/60	2.80	0.44
	trans-Butene-2	+0.9	20/60	3.55	0.56
	cis-Butene-2	+3.7	20/60	4.00	0.62
5	Pentene-1	+30.0	20/60	7.15	1.12
	Hexene-1	+63.5	20/60	18.7	2.92
6	*trans*-Pentene-2	+36.3	20/60	8.70	1.36
	cis-Pentene-2	+36.9	20/60	9.30	1.45
	trans-Hexene-2	+67.9	20/60	21.1	3.30
	cis-Hexene-2	+68.8	20/60	23.4	3.66
7	Propadiene	−34	20/60	2.25	0.35
	Butadiene-1,3	−4	20/60	3.95	0.62
	2-Methylbutadiene-1,3	+34	20/60	10.8	1.70
8	Acetylene	−84	20/60	0.90	0.14
	Propyne	−23	20/60	2.90	0.45
	Butyne-1	+8	20/60	6.30	0.98
Misc.	Air	—	20/60	(1.40)	0.00
	Carbon monoxide	−190	20/60	0.00	0.00
	Carbon dioxide	−78	20/60	0.25	0.04
	Neopentane	+10	20/60	2.65	0.41
	Isooctane	+99	20/60	37.8	0.59

RETENTION DATA, COLUMN R—*Continued*

Polypropylene glycol (UCON LB-550-X), 20% by weight on 60–80 mesh Chromosorb; length: 4 meters, temperature 100° C

Mix no.	Component	Boiling point, °C	P/F	T_r, min (air = 0)	Ratio (nC_5 = 1)
1	Methane	−162	20/46	0.10	0.04
	Ethane	−89	20/46	0.30	0.11
	Propane	−42	20/46	0.60	0.21
	Butane	−0.5	20/46	1.35	0.48
2	Pentane	+36	20/46	2.80	1.00
	Hexane	+69	20/46	5.70	2.04
	Heptane	+98	20/46	11.6	4.14
	Octane	+126	20/46	24.2	8.35
3	2-Methylpropane	−12	20/46	0.95	0.34
	2-Methylbutane	+28	20/46	1.90	0.68
	2-Methylpentane	+60	20/46	4.15	1.48
4	Ethylene	−104	20/46	0.20	0.07
	Propylene	−48	20/46	0.60	0.21
	Isobutene	−6.9	20/46	1.35	0.48
	Butene-1	−6.3	20/46	1.35	0.48
	trans-Butene-2	+0.9	20/46	1.65	0.59
	cis-Butene-2	+3.7	20/46	1.80	0.64
5	Pentene-1	+30.0	20/46	2.80	1.00
	Hexene-1	+63.5	20/46	5.80	2.07
6	*trans*-Pentene-2	+36.3	20/46	3.25	1.16
	cis-Pentene-2	+36.9	20/46	3.50	1.25
	trans-Hexene-2	+67.9	20/46	6.60	2.36
	cis-Hexene-2	+68.8	20/46	7.10	2.54
7	Propadiene	−34	20/46	1.20	0.43
	Butadiene-1,3	−4	20/46	1.85	0.66
	2-Methylbutadiene-1,3	+34	20/46	3.75	1.34
8	Acetylene	−84	20/46	0.50	0.18
	Propyne	−23	20/46	1.65	0.59
	Butyne-1	+8	20/46	2.50	0.89
9	Benzene	+80	20/46	18.2	6.52
	Toluene	+111	20/46	37.4	13.4
	Ethylbenzene	+136	20/46	69.0	24.6
	p-Xylene	+138.4	20/46	76.0	27.1
	m-Xylene	+139.1	20/46	76.0	27.1
	o-Xylene	+144.4	20/46	92.1	32.9
	Isopropylbenzene	+152	20/46	102.0	36.4

RETENTION DATA, COLUMN R—*Continued*

Mix no.	Component	Boiling point, °C	P/F	T_r, min (Air = 0)	Ratio ($nC_5 = 1$)
10	Cyclopentane	+49	20/46	5.20	1.86
	Methylcyclopentane	+72	20/46	8.20	2.93
11	Cyclohexane	+81	20/46	11.2	4.00
	Methylcyclohexane	+101	20/46	16.9	6.05
12	Methanol	+65	20/46	8.9	3.18
	ethanol	+78	20/46	8.9	3.18
	Propanol	+97	20/46	18.6	6.64
	Butanol	+118	20/46	40.0	14.3
13	2-Propanol	+82	20/46	9.8	3.52
	2-Butanol	+100	20/46	20.1	7.18
14	*tert*-Butyl alcohol	+83	20/46	8.4	3.00
	tert-Amyl alcohol	+102	20/46	20.2	7.21
15	Acetaldehyde	+20	20/46	2.7	0.96
	Propionaldehyde	+50	20/46	5.0	1.80
	Butyraldehyde	+75	20/46	10.3	3.68
	Valeraldehyde	+103	20/46	21.6	7.71
16	Acetone	+56	20/46	5.6	2.00
	2-Butanone	+80	20/46	11.4	4.07
	2-Pentanone	+103	20/46	21.1	7.54
	2-Heptanone	+150	20/46	86.1	30.8
17	Methyl acetate	+58	20/46	6.8	2.41
	Ethyl acetate	+77	20/46	11.6	4.12
	n-Propyl acetate	+102	20/46	21.8	7.79
	n-Butyl acetate	+126	20/46	44.9	16.0
18	Diethyl ether	+35	20/46	3.6	1.29
	Diisopropyl ether	+68	20/46	6.2	2.21
	Di-*n*-butyl ether	+138	20/46	50.7	18.1
Misc.	Air	—	20/46	(1.60)	0.00
	Carbon monoxide	−190	20/46	0.00	0.00
	Carbon dioxide	−78	20/46	0.25	0.09
	Neopentane	+10	20/46	1.30	0.46
	Isooctane	+99	20/46	10.60	3.80
	Water	+100	20/46	14.80	5.29

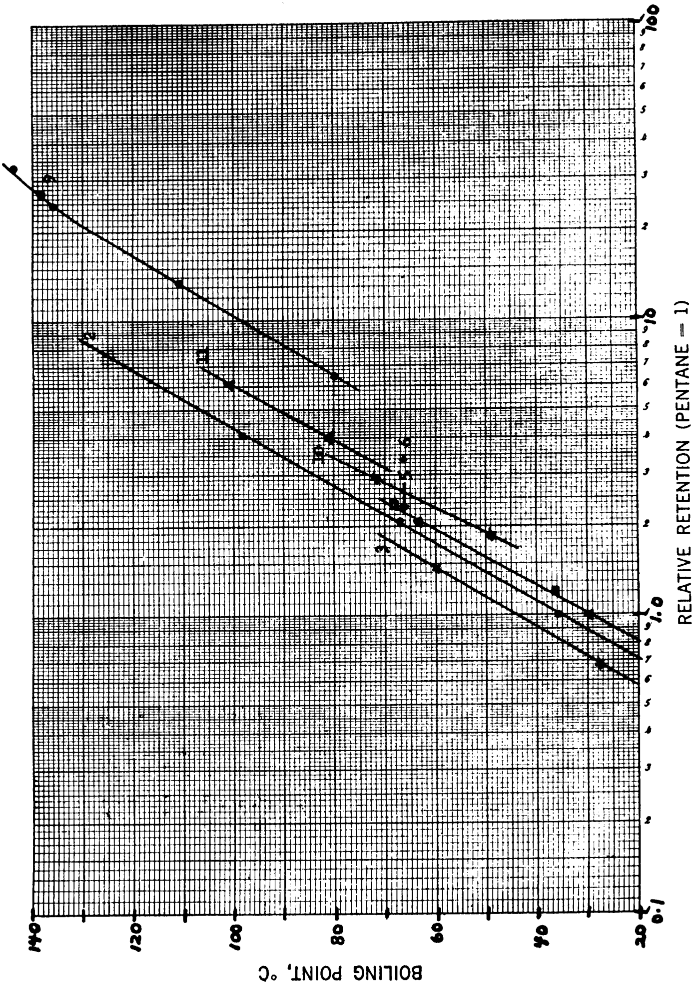

FIG. 16. Separation of hydrocarbons on polypropylene glycol (R) at 100° C.

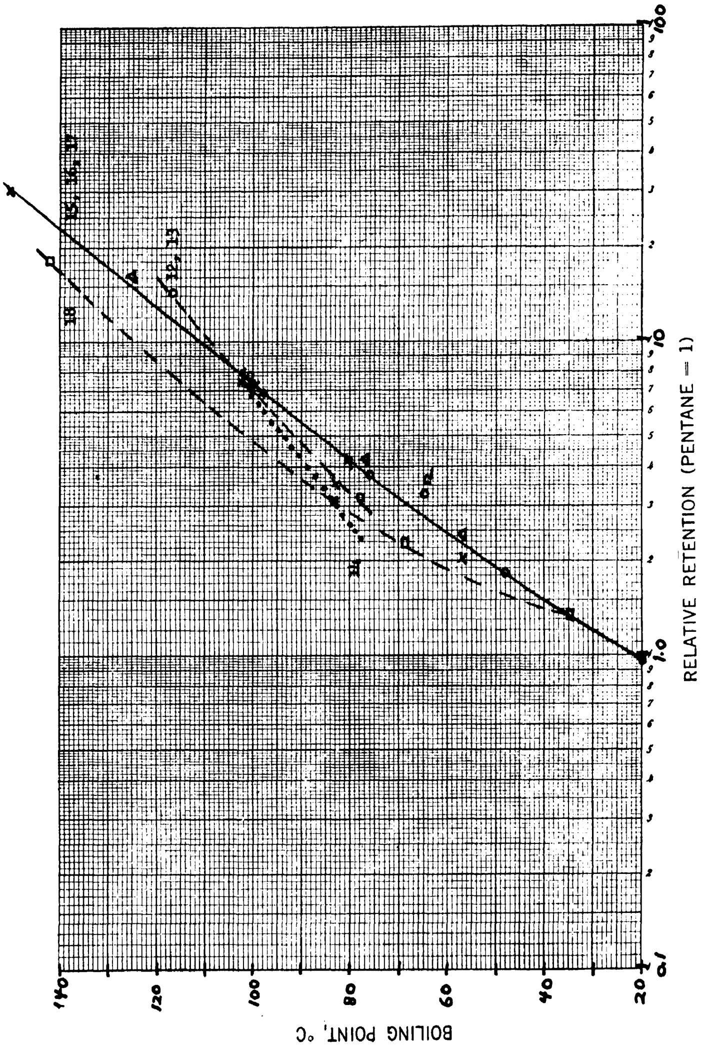

FIG. 17. Separation of oxygenated compounds on polypropylene glycol (R) at 100° C.

SUMMARY

Eighteen mixes representing a wide variety of chemical types were run at 100° C on eight standard partition columns; namely, diisodecyl phthalate, di-2-ethylhexyl sebacate, silicone oil D. C. #200, silicone grease, Carbowax 1500, polydiethylene glycol succinate, Apiezon "L" hydrocarbon grease, and UCON polyglycol LB-550-X. Eight light hydrocarbon mixes were run in addition at a temperature of 50°C on the above-mentioned columns. The retention data have been presented both in tabular form and in the form of graphs of relative retention values plotted logarithmically against the boiling points of the standard mixture components. Additional retention data were also presented on two partition materials used for special applications.

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CHAPTER XXVI

Trace Analysis for Impurities in Hydrocarbon Concentrates

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This paper describes the special requirements for gas chromatography columns, detectors, recorders, and operational controls as applied to trace analysis. The applications on which this experience is based have been related largely to the determination of trace impurities in petrochemicals or in hydrocarbon mixtures derived from petroleum, but the same techniques are useful in the trace analysis of any compounds which can be vaporized without decomposition or reaction with the gas chromatography (GC) apparatus.

CHROMATOGRAPHIC COLUMNS

The GC columns which have proven to be the best for macro separations have been found to be also the choice for trace determinations. A "good" column should resolve all components of interest of a single type and C number or narrow boiling range. Also, the separation of peaks must be maximum in order that a signal from a trace component will not be lost in the signal from an adjacent major component. An example from such a typical superior column is the chromatogram shown in Fig. 1. This column contains benzyl Cellosolve, one of the solvents useful for separation of olefins. The kind of solvent is often not so important as the column dimensions, treatment of the packing, and operating parameters. A good illustration of this point was noted in the comparison of several solvents intended for olefins separation. The solvents chosen are structurally quite different; in fact, these materials are diverse in most respects other than the presence of strong functional groups. As may be noted in Fig. 2, each of the compounds gave good separation of two C_5 olefins, which boil 1.1° F apart, and similar satisfactory separation, as shown in Fig. 3, of two C_6 olefins boiling only 0.6° F apart. It will be noted also that in each case the olefins are eluted in the same order.

By careful operation of a conventional laboratory GC apparatus, it is possible to analyze for concentrations as low as 1 ppm without the complication of freeze-out or other techniques for concentrating the desired components. Figure 4 shows an example of such application. A sensitive detector used in conjunction with a 1.0-mv full scale recorder and a gas sample as

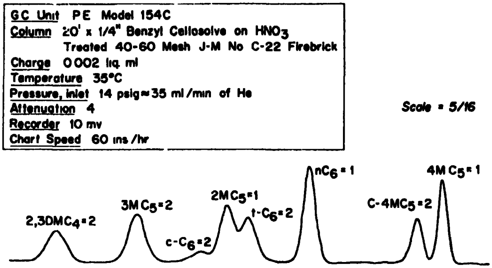


FIG. 1. Separation of hexenes by gas chromatography.

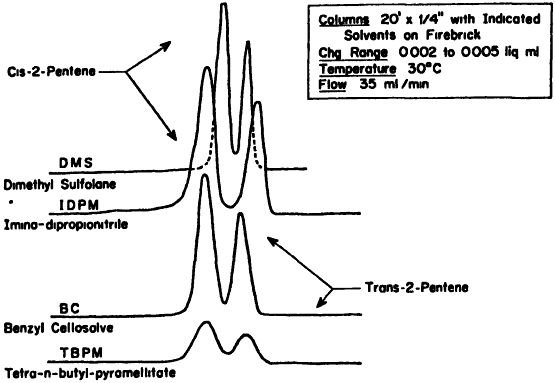


FIG 2. Comparison of substrates for separation of pentenes by gas chromatography.

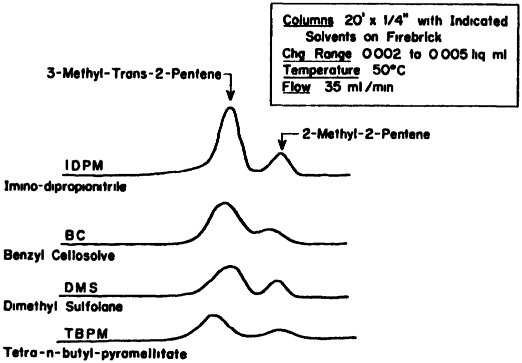
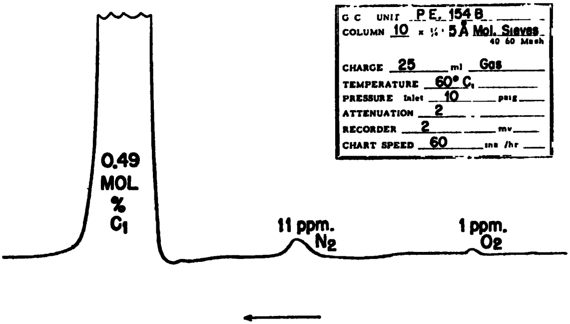


FIG. 3. Comparison of substrates for separation of hexenes by gas chromatography.

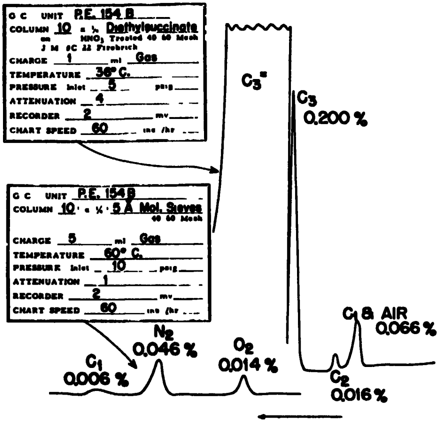
small as 25 ml will give a readily measurable peak for any 1-ppm component which gives a roughly symmetrical peak at the operating conditions used. The same amplification would permit the measurement of as little as 2.5 ppb of a condensible from a 10-liter air or vapor sample.

Trace techniques serve to call attention in very graphic fashion to the presence and amounts of impurities in nominal pure hydrocarbons, as shown in Fig. 5. This is a useful tool for checking the purities of standards used to calibrate routine test methods, for controlling the purities of materials charged to reforming operations, and in making specification tests



G C UNIT P E. 154 B
COLUMN 10 × ¼′ 5 Å Mol. Sieves 40 60 Mesh
CHARGE 25 ml Gas
TEMPERATURE 60° C.
PRESSURE Inlet 10 psig
ATTENUATION 2
RECORDER 2 mv
CHART SPEED 60 ins /hr

FIG. 4. Gas chromatography analysis of purchased ethylene.



G C UNIT P.E. 154 B
COLUMN 10 × ⅛ Diethylsuccinate on HNO₃ Treated 40 60 Mesh J M #C 22 Firebrick
CHARGE 1 ml Gas
TEMPERATURE 36° C.
PRESSURE Inlet 5 psig
ATTENUATION 4
RECORDER 2 mv
CHART SPEED 60 ins /hr

G C UNIT P.E. 154 B
COLUMN 10′ × ¼′ 5 Å Mol. Sieves 40 60 Mesh
CHARGE 5 ml Gas
TEMPERATURE 60° C.
PRESSURE Inlet 10 psig
ATTENUATION 1
RECORDER 2 mv
CHART SPEED 60 ins /hr

FIG. 5 Gas chromatography analysis of research grade propylene (nominal purity 99.72).

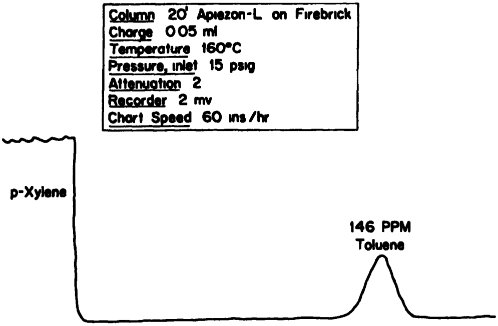


FIG. 6. Gas chromatography analysis of trace toluene in xylene.

on petrochemical products. The technique is applicable also to the higher boiling ranges. As a substitute for the loss of sensitivity of most thermistors at elevated temperatures, the hot wire or katharometer type detector may be useful. If sensitivity is too low this disadvantage often may be offset by using a larger diameter column and charging a correspondingly larger sample. An example of this approach is indicated in Fig. 6.

There is frequent need to determine traces of non-hydrocarbons in petroleum fractions. Concentration of the suspected trace contaminant by distillation may not be feasible because of azeotrope formation. By careful choice of GC techniques it is often possible to accomplish the desired separation. A typical illustration is included in Fig. 7. In this instance the total chloro compounds found by GC amounted to 6 ppm as compared to 8 ppm by an independent chemical method.

In a recent evaluation of 24 different 10-20 ft columns to determine what constitutes a superior column, the determination of the theoretical plate equivalents of these columns indicated that the best columns ranged from 152–234 plates/ft, whereas the inefficient columns ranged from 71–118 plates/ft. The 2-sigma significance of these numbers is about 5.0 plates/ft. As an indication of the accuracy and precision at the trace levels for hydrocarbon determinations, the standard deviation (repeatability) for several C_3-C_4 hydrocarbons in the 15–50 ppm range was found to be <1–2 ppm and the average deviation from synthesis composition was 0–3 ppm.

DETECTORS

Although the proper design and preparation of GC columns is important, since sharp resolution of a trace component must be realized before it can be amplified and measured, the necessity of a sensitive detector-bridge-recorder system is obvious. In order to visualize the parameters which

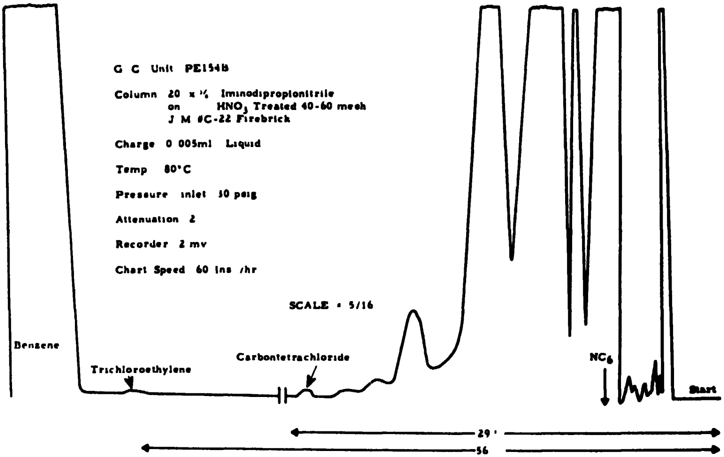


FIG 7 Gas chromatography test of 157–168° F fraction from LCN for chlorinated additives.

must be maximized, it has been helpful to refer to the fundamental expressions for filament and thermistor detectors. The familiar formula from Keulemans' textbook (*1*) is useful and is reproduced below as a matter of reference.

$$E = \frac{1}{4} I \cdot IR_{t_w} \cdot \frac{\alpha(t_w - t_c)}{1 + \alpha t_w} \cdot \epsilon \cdot \frac{2\gamma}{1 + \gamma}$$

E = out of balance voltage of the bridge
I = total bridge current
R_{t_w} = resistance of the wire at its own mean temperature
α = an instrument constant
t_w = mean temperature of wire
t_c = temperature of cylinder wall
ϵ = relative change in thermal conductivity due to a mole fraction of vapor in the carrier gas
γ = ratio of the resistances in the wheatstone bridge

Inspection of this formula suggests some obvious recommendations, including maximum bridge current, high resistance for the filament, and arrangement of the sensing element, heat sink and thermostat to give a maximum temperature difference. The response of thermistor detectors is more complex but an excellent rigorous derivation was presented by Stirling and his colleagues in their ISA paper (*2*). The comprehensive relation as derived by Stirling is included here for reference.

$$\xi = \frac{e^{-b/2T}\cdot e^{b/2(T+\theta)}\cdot b\theta^{3/2}}{2(T+\theta)^2}\cdot\sqrt{R_0\cdot\pi\cdot J\cdot D\cdot K_f\cdot Nu_f}\cdot\frac{\delta k}{k}$$

ξ = open circuit detector voltage due to changes in thermal conductivity
b, K_f, and Nu_f are constants.
T = ambient temperature, ° C
θ = temperature difference between body and surroundings, ° C
R_0 = electrical resistance of body at $T + \theta$, in ohms
k = thermal conductivity of the ambient fluid, cals/(cm^2) (sec) (° C temp. difference/cm)
J = electrical equivalent of heat, watts/cal
D = characteristic dimension of body, cm

How to control the thermistor for maximum signal may not be readily apparent, but Stirling's data indicate a current range of 5–10 ma and a temperature difference of 30–60° C are desirable. Also, the most sensitive thermistors had the highest resistance.

As indicated previously, thermistors are preferred to the filament type detector for trace work, except at high temperature. In addition to higher sensitivity, thermistors have a better signal/noise ratio by a factor of about 5. The long-term drift is about the same for both types. Another advantage of the thermistor is the small volume requirement. This is essential if close boiling trace components of the same type hydrocarbon are to remain separated.

For trace applications the time for full response should not be over 2 sec and preferably 1 sec or less. Cell geometry has an important bearing on this feature. The full diffusion type should not be used and the straight through type may be noisy. Some compromise, as in the Gow-Mac pretzel type, may be best.

Independent heater circuits on the detector and column make it possible to establish a favorable temperature difference between sensing element and heat sink. Thermistor temperature usually is not over 150° C, whereas tungsten or other filaments may operate near the glow point. A typical thermistor requires up to about 10 ma in He as compared with a much wider range of about 100–350 ma of filament current for the hot wire type. The most dependable current supply is a 6- or 12-volt wet battery although dry batteries are popular in commercial instruments. A good current control will be noise free. In this connection the total random noise of a thermistor should be less than 20 μv and likewise the random drift for 30 minutes should be 20 μv maximum. Sustained drift, 1 hour or longer, may be expected to be not over 30 μv per hour. The bridge circuit should be short and symmetrical using matched resistances ±1 % or better. These resistors should have high resistance; 500–1200 ohms has been typical.

RECORDERS

Recorder specifications are critical in trace work. Some of the features to be considered are the following:

1. Sensitivity
2. Pen speed
3. Chart speeds
4. Automatic standardization
5. Electrical shielding
6. Gain control
7. Limit of error

There should be no compromise on sensitivity or pen speed; 1-mv full scale signal and 1-sec pen speed are desirable. Two chart speeds are useful, one of 30 or 60 inches per hour for separations of material boiling up to about 300° F, and a speed in the range of 4–12 inches per hour for high temperatures. Automatic standardization is important since it minimizes base line drift and improves the accuracy of quantitative measurements. The amplifier should be the high gain, low level type. This usually uses 5 stages of amplification with the gain control at the second stage. Careful adjustment of the gain serves to minimize the dead band without increasing random noise. The limit of error should not be greater than ±0.3% of the range span. This is equivalent to 2 or 3 pen line widths. All connections in the calibrated circuit, i.e., slidewire, resistors, standard cell, and temperature compensator, must be soldered, not plug-in or screw-in types.

SAMPLE CHARGING

Turning now to some of the accessories needed in trace analysis, an accurate and dependable sample charging device must be available. Calibrated 4-way valves for gas samples are available from several suppliers and reports on most of these are satisfactory. In this laboratory a popular liquid charging device was made by modifying a Gilmont Micropipet-Buret (*3*).* The appearance of the modified device after re-assembly is shown in Fig. 8. The more recent models have a counter type read-out head instead of the dial type, but the modification and application are the same. Also, the manufacturer, The Emil Greiner Company, now supplies a glass part for the Luer type fittings. This can be ordered separately,

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* *Note:* This reference describes an early model which differs in design from the model referred to in this paper.

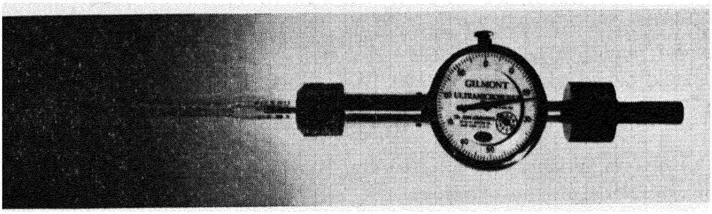

FIG. 8. Liquid sample charging device.

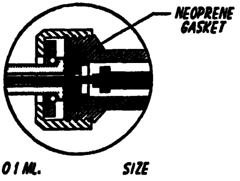

FIG. 9. Detail of coupling assembly.

thus eliminating the need to cement a needle into the standard glass part. In any event, the packing section should have installed in it an additional close fitting gasket of neoprene or similar material to prevent back pressure leakage, as indicated in Fig. 9. The ruby plunger is rather fragile and not intended for operation through a tight fitting gasket. In practice it is best to replace the plunger with a stainless steel rod of the same dimensions. The modified charging device affords the advantage of wide range of volumes, from <0.001 to >1.0 ml., with selection of any intermediate volume, and dispenses all liquid hydrocarbons up to heavy oils regardless of viscosity or surface tension properties. The reproducibility of charging samples is satisfactory as indicated by Fig. 10. The reproducibility of the peak height was found to vary only ±0.3 to ±0.5% in the back pressure range of 5 to 15 psig.

OTHER INSTRUMENT CONTROLS

Other controls to check are temperature and flow rate, since these become increasingly important as sensitivity and amplification are increased. Temperature variation should be less then ±0.1° C. The Model S Thermonitor of E. H. Sargent & Company has proven quite satisfactory. In using this instrument the metal shield should be removed from the thermistor element when it is installed in order to reduce time lag of the response. An on-off single heater circuit is to be avoided. An auxiliary small (ca. 25 watts)

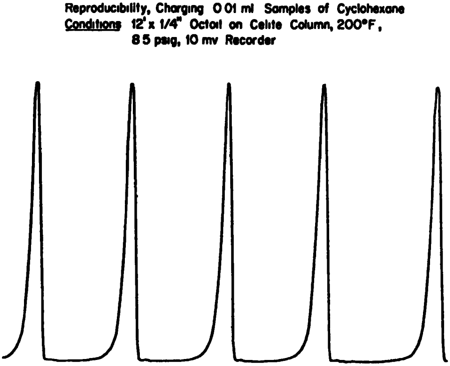

Fig. 10. Reproducibility of liquid charging in gas chromatography.

cycling heater should be included. Insulation on most laboratory units is inadequate for installations outside of air conditioned rooms. The flow control should be sufficient to hold the desired rate within ±1%.

In conclusion, for the information of those who may have just begun the application of GC to trace analytical problems, given below is a list of instrument variables which are the more common causes of faulty operation. Of these, Nos. 1, 2, 6, 8, and 9 are the most frequent sources of trouble.

1. Dirty detector unit
2. Inadequate temperature control
3. Faulty pressure regulator
4. Fluctuations in detector current
5. Broken, burned, or corroded detector element
6. Corroded gain controls or other switch contacts, including dirty slide wire in recorder
7. Improperly adjusted recorder gain control
8. Loose connections in bridge circuit
9. Obstructions in flow lines, such as pieces of packing or gasket material, stopcock grease, condensate in rotameter, high melting components in exit line

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CHAPTER XXVII

Gas Chromatographic Separations of Close Boiling Isomers

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The unique ability of gas chromatography to readily separate complex organic mixtures into their individual components has been responsible for its widespread use. Several isomeric components, however, have proved to be quite difficult to resolve. The isomers of xylene, cresol, and diisopropyl benzene are examples of this problem. At the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in March, 1959, the separation of ortho-, meta-, and para-xylene was described. A capillary column and an ionization detector were employed in that case and the exceptional resolution obtainable with the Golay columns was well illustrated. The work which I shall describe in this paper uses the older, more conventional packed columns. It is illustrative, however, of the remarkable separatory powers obtainable by the proper choice of column materials and operating conditions.

The isomers of diisopropyl benzenes (DIB) have been an analytical problem for some time. This is due to the fact that pure samples of the ortho and meta forms were very difficult to obtain for use in either mass spectrometric or infrared calibrations. The boiling points in the literature (*1*) for these compounds are: *m*-DIB, 203.18° C; *o*-DIB, 203.75° C; *p*-DIB, 210.37° C.

A chromatogram of these solutions generally shows only two peaks, since the ortho and meta forms have essentially the same boiling point. Using a 5-m column of Chromosorb, 30–40 mesh, coated 10% by weight with dicarbitol phthalate, a complete separation of the three isomers is obtained. The retention times at a temperature of 135° C and an applied pressure of helium of 15 psi were 19, 21, and 23 minutes, respectively, for the meta-, ortho-, and para-isomers. This separation is illustrated in Fig. 1.

The Perkin-Elmer model 154-B was used in this study. To obtain the maximum resolution from the instrument it was necessary to increase the heat applied to the injection chamber. This was done by putting a 100-watt strip heater in place of the one furnished with the instrument. A thermocouple was also attached to the block to measure the temperature. The strip heater was powered by a separate variac. Using this arrangement it was possible to vaporize the sample instantaneously by having the injection chamber at 250° C while the oven was only at 135° C. This lessens any tendency of peaks to broaden in the injection chamber due to slow vaporization. The instrument as furnished was equipped with a 5-mv recorder. To obtain more sensitivity and thus permit the introduction of smaller samples the range was changed to approximately 1 mv. This can be done very readily by applying the voltage from the dry cell of the recorder to a potentiometer and using only approximately 0.3 volt. A further increase in sensitivity was obtained by applying 10 volts to the thermistor bridge instead of the normal value of 8. These changes increased the sensitivity of the instrument about ninefold. The changes made in the recorder and in heating of the injection block are the major factors in the increased resolution. We were unable to obtain complete separation prior to making these changes because of the size of the sample required.

The separation of the isomers of cresol is of considerable interest to those working in the tar acid field. In this case the meta- and para-isomers are the ones more difficult to resolve. Their boiling points are given in the literature (*2*) as para-cresol, 201.9° C, and meta-cresol, 202.7° C. Usually these compounds are found in the "light cresol cut" in the presence of phenol. Our attempts at separation were therefore done on a mixture of phenol, and ortho-, meta-, and para-cresol. The polarity of these compounds is a further

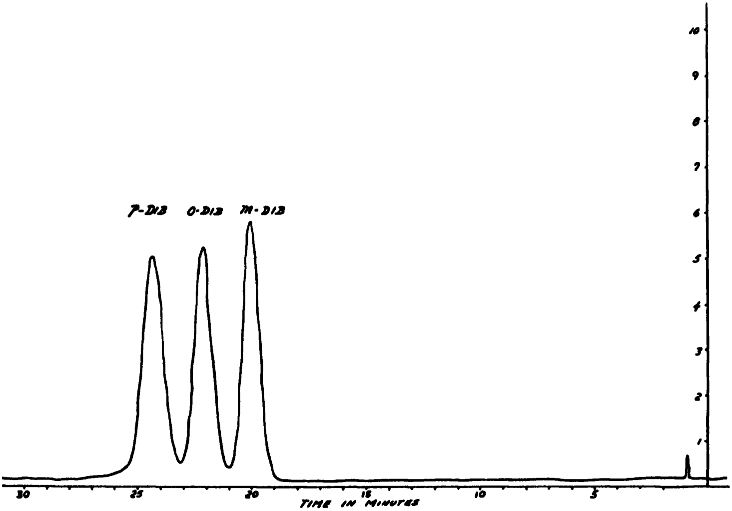

FIG. 1. Chromatogram showing complete separation of the meta-, ortho-, and para-isomers of diisopropyl benzene. Column: 5 meters 10% dicarbitol phthalate; carrier gas helium, 15 psi; oven temperature: 135° C; block temperature. 250° C.

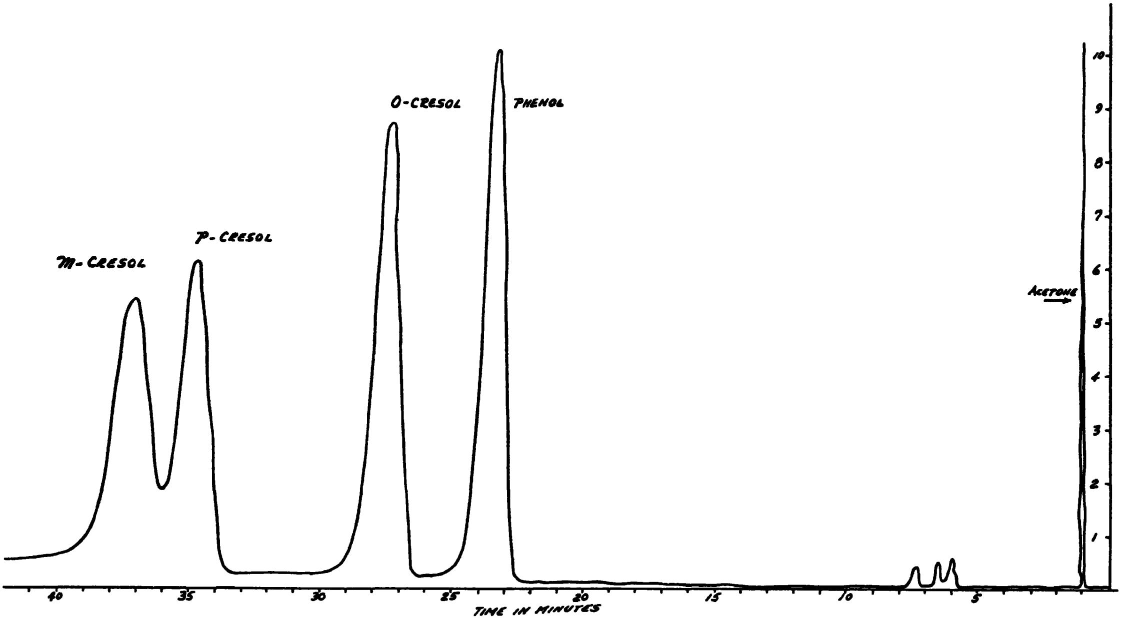

FIG. 2. Chromatogram showing complete separation of the meta-, ortho-, and para-isomers of cresol Column: 4 meters 5% TCP-3% H_3PO_4 ; carrier gas· helium, 35 psi; oven temperature 140° C; block temperature. 250° C

difficulty that is encountered, since this factor generally increases adsorption and produces peaks with "tails." Our investigation resulted in the choice of a combination of tricresyl phosphate (TCP) and phosphoric acid as a partitioning medium. The phosphoric acid helps to prevent tailing of peaks and also plays some part in the separation, presumably by greater hydrogen bonding. Neither substance will effect the separation by itself. The proportions used were 3 to 5% H_3PO_4 and 5% TCP based on the weight of 40–50 mesh Chromosorb used. The typical chromatogram obtained is shown in Fig. 2. Other proportions of the partitioning liquids were found to be less effective. A 4-meter column was employed in this case and an inlet pressure of 35 psi. This resulted in retention times of 22 minutes for phenol, 26.3 minutes for ortho-cresol, 33.8 minutes for para-cresol, and 36 minutes for meta-cresol. The tricresyl phosphate used was the ortho form. This was verified by infrared

In conclusion, I should like to point out that the above examples show that by the proper choice of column materials and experimental conditions one can still perform some very difficult separations with the old-fashioned packed column and the relatively inexpensive thermal conductivity cell.

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CHAPTER XXVIII

Separation of Some Mixtures of Isomeric Organic Compounds by Gas Chromatography

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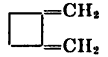
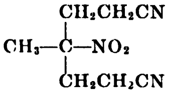
Mixtures of isomeric organic compounds have been separated by gas chromatography on two new liquid adsorbents of remarkable selectivity. These separations were accomplished on a scale sufficient for limited chemical studies of the products through use of a simple large-scale apparatus readily constructed from available materials. Each of the mixtures discussed was not separable by fractional distillation.

The isomeric dimers of allene, 1,2-dimethylenecyclobutane (I), b.p. 74° C, and 1,3-dimethylenecyclobutane (II), b.p. 68.5°–69° C, (*1*) are difficult to separate by gas chromatography. Tide is the only one of the better-known adsorbents able to separate the compounds. We have found that 3-methyl-3-nitro-1,5-dicyanopentane (III; *2*) and the tris-β-cyanoethyl derivative of glycerol (IV; *3*) show remarkable selectivity for this type of compound.



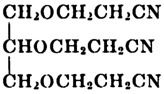
(I)

(II)



$$\begin{array}{l} \quad\;\; CH_2CH_2CN \\ \quad\;\; | \\ CH_3-C-NO_2 \\ \quad\;\; | \\ \quad\;\; CH_2CH_2CN \end{array}$$

(III)

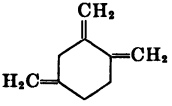


$$\begin{array}{l} CH_2OCH_2CH_2CN \\ | \\ CHOCH_2CH_2CN \\ | \\ CH_2OCH_2CH_2CN \end{array}$$

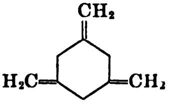
(IV)

When compound (III) was used on firebrick in a 6 ft × ¾ inch column at 50° C, 2-ml samples of the mixture were separated at 30-min intervals. A recorder chart of one of these separations is reproduced as example I, Fig. 1.

The separation of the allene trimer, 1,2,4-trimethylenecyclohexane (V) and 1,3,5-trimethylenecyclohexane (VI; *4*), also difficult using other



(V)



(VI)

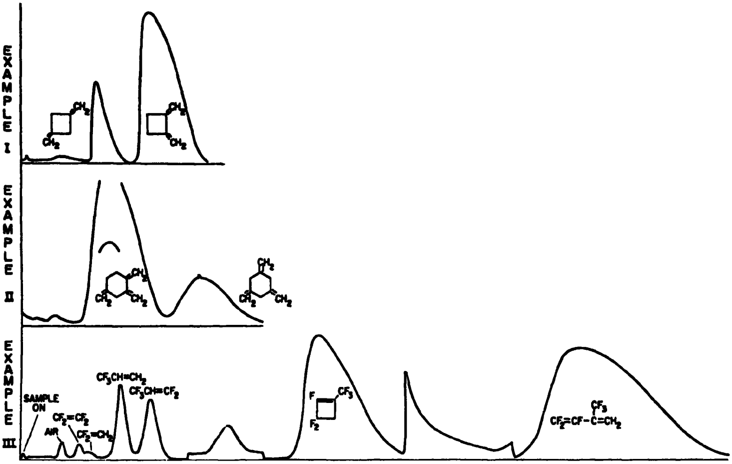
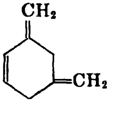


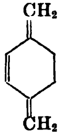
Fig. 1. Recorder chart of separation of isomeric organic compounds.

adsorbents, was possible using the column described above but operating at the temperature limit of this liquid phase, which is 100° C. A recorder chart of this separation is reproduced as example II, Fig. 1.

In a similar manner, 3,5-dimethylenecyclohexane (VII) can be separated from 3,6-dimethylenecyclohexene (VIII; *5*) on the same column at 100° C.



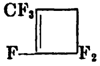
(VII)



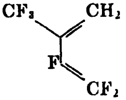
(VIII)

Although the nitrodinitrile (III) appears to be more selective and versatile than the glyceryl ether (IV), the latter's useful temperature range is higher, extending to 150° C. Both of these liquids are limited by decomposition rather than volatility.

The separation of 1-trifluoromethyl-2,3,3-trifluorocyclobutene (IX), b.p. 34° C, from 1,1,2-trifluoro-3-trifluoromethyl-1-1,3-butadiene (X),



(IX)



(X)

b.p. 38° C (*6*), is readily accomplished on a 6 ft × 2 inch column of silicone oil on firebrick at room temperature. This mixture, which cannot be separated by distillation because of the tendency of the diene to polymerize, can be separated in 12-g batches with a 20-min cycle time, so that the throughput of this column for this mixture is large. A recorder chart of one of these separations is reproduced as example III, Fig. 1.

From these experiments we have gradually evolved a relatively simple column design for routine use in separating and purifying volatile organic chemicals. Because the column is simply fabricated from readily available parts it is described here (Fig. 2).

The column consists of two 6-ft lengths of ¾ annealed copper pipe

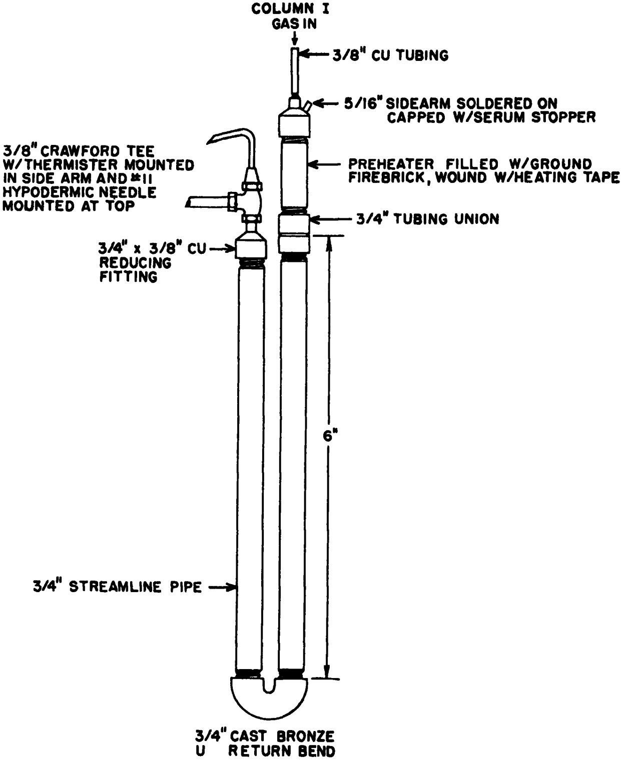


FIG. 2. Gas chromatography column.

soldered in a ¾ in cast bronze U-return bend. The inlet side is connected by means of a Crawford tubing union to a 1 ft section of ¾ inch pipe which serves as a preheater. A ¾ × ⅜ copper reducing fitting is soldered to the preheater and outlet sides of the column. The helium supply is connected on the inlet side, and samples are injected through a length of 5/16 inch copper tubing soldered into the reducing fitting and capped by a serum stopper. The ⅜ inch outlet of the column is connected to a ⅜ inch Crawford tubing tee into which a single Victory Engineering A-111 thermistor and the Luer-Lok portion of a syringe are mounted by friction (Fig. 3). A curved hypodermic needle attached to the Luer-Lok serves as the outlet. The thermistor is wired as one arm of a Wheatstone bridge and balanced by means of a suitable variable resistor.

The column is heated by immersion in an air bath, and the preheater is wrapped with heating tape. Sample injection is by hypodermic syringe.

The performance of this column is adequate for the separations described, although it is not as efficient as analytical columns. For example, in the

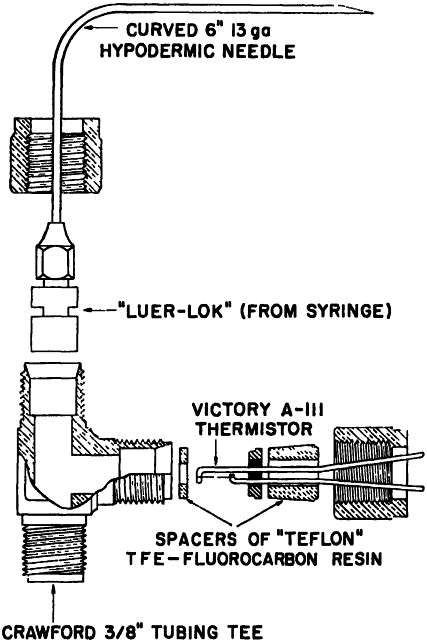


FIG 3. Thermal conductivity cell.

separation of compounds (VII) and (VIII), plate values were 945 and 1020, respectively, when this column was packed with 3-methyl-3-nitro-1,5-dicyanopentane on 38-65 mesh firebrick at a helium flow of about 300 ml/min, temperature: 95° C, and 1-ml sample size. No attempt was made to find optimum conditions.

Many variations of the design described above are possible, but the simple arrangement described here has proved very adequate for most separations. Substitution of a simple two-thermistor thermal conductivity cell for the single thermistor adds to useful sensitivity by improving base-line stability. Use of manifold systems for sample collection is possible but adds little except in special cases.

Samples are collected in traps connected to the column outlet by serum stoppers. Figure 4 contains drawings of three types of traps which we have

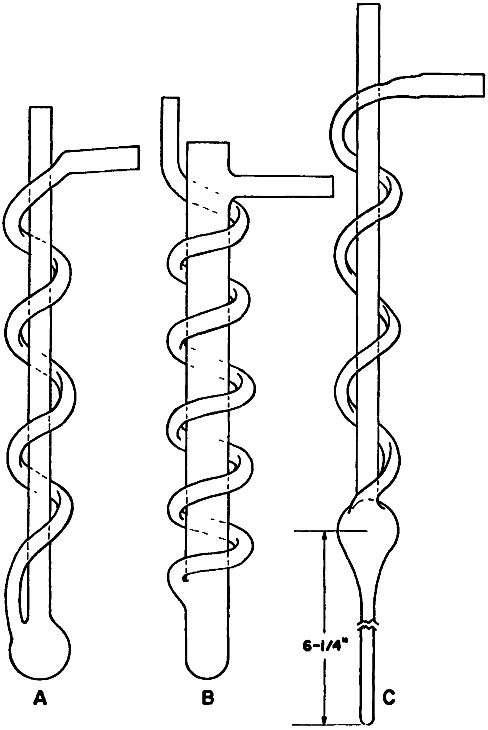


FIG. 4. Cold traps

found useful in this sort of work. Trap A is a conventional spiral trap for readily condensable liquids. Trap B is useful for large quantities of materials which crystallize in the cooling bath being used. Trap C is useful for obtaining n-m-r spectra of fractions collected in small amounts and also for sealing pure samples of compounds that are sensitive to oxygen or moisture into ampules.

Analytical results on samples collected in traps such as C and sealed into the smaller tubing have been uniformly good.

ACKNOWLEDGMENT

The author is indebted to Dr. E K. Ellingboe of this laboratory for design of the single thermistor sensing device described here

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Chapter XXIX

The Determination of Halogenated Hydrocarbons by Gas Chromatography and Flame Photometry

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In industrial health work it is desirable to be able to separate and identify the more toxic constituents of solvents and dry-cleaning fluids. Among such toxic materials commonly encountered are chlorinated hydrocarbons. Individual members of this class of most frequent occurrence are carbon tetrachloride, methyl chloroform, methylene chloride, trichlorethylene, perchlorethylene, and ethylene dichloride.

The separation and quantitative determination of such chlorinated hydrocarbons, in known mixtures, has become rather easy by using gas chromatography (*1*). For the complex unknown solvent mixtures encountered commercially it would be helpful to be able to identify all peaks on the chromatogram due to chlorinated hydrocarbons. This may be done by a simple application of the Beilstein test for chlorine in organic compounds (*2*).

These workers introduce the effluent from the chromatographic column into a simple glass burner having a copper wire helix mounted in the flame. When the column effluent entering the burner contains a chlorinated hydrocarbon a green color is imparted to the flame momentarily. This test is quite sensitive as it stands, although probably the sensitivity could be increased by improved burner design. It is necessary, of course, for the operator to be present to make the observations and correlate the positive test for chlorine with the relevant peak.

Since in our laboratory, as in many others, it is necessary for the analyst to double in brass, we have made this identification of halogens automatic and concurrent with the usual recording of the gas chromatogram. This is illustrated in a block diagram (Fig. 1). While the chromatogram is recorded in the usual way, the effluent gas enters the burner of a flame photometer having a copper element in the burner. The output from the flame photometer, instead of being read on the built-in meter, is fed into a second recorder. This second recorder shows a peak only when a halogenated compound enters the flame. Comparison of the two recorder charts indicate which of the original peak components contains a halogen.

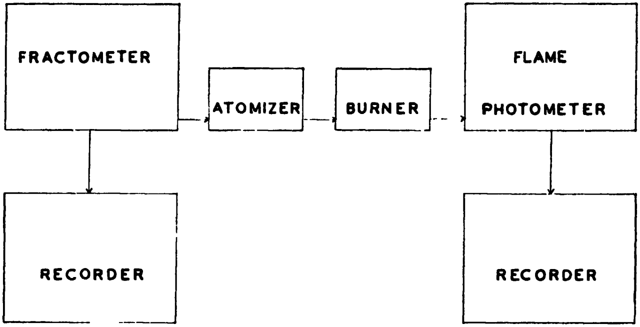

FIG 1 Block diagram

APPARATUS

We have used Perkin Elmer Fractometers Models 154A and 154C for the gas chromatographic separations. No attempt was made to select columns specially suited to halogenated hydrocarbons. We considered this unnecessary since the samples encountered, as already mentioned, might contain any or all of alcohols, esters, ketones, aromatics, and aliphatics in addition to the halogenated compound. We used Column A phthalate ester in a 1-meter length column with thermistor-type thermal conductivity detectors. Other operating parameters were temperature 80° C, and inlet pressure 10 psig helium.

The flame photometer was made by Dr. Bruno Lange, West Berlin, Germany. This instrument is designed for use with natural or coal gas from the mains. It can also be operated with greater sensitivity, using the built-in compressor and a gasoline generator. Air is used as the source of oxygen. This instrument was ordinarily operated at a gage pressure of 0.4 g/sq cm. The filter used was the 520-mm interference filter supplied.

The burner of the Lange instrument consists of a vertical glass cylinder 20 mm OD. Upon the plane ground top opening of the burner rests a uniformly perforated aluminum plate which is held in place by a shouldered stainless steel ring which drops down over the plate and glass cylinder.

Limited experimentation was carried out to devise a suitable copper element for this burner. The design finally chosen is shown in Fig. 2. This consists of a one-piece ring and plate of rather massive construction which is simply dropped into place over the glass chimney after removal of the aluminum plate and steel ring. This copper element was

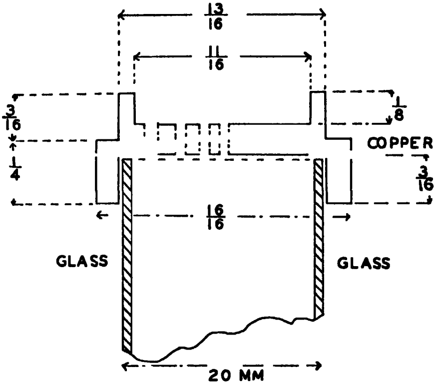

FIG. 2. Detail of burner.

turned on the lathe from electrolytic copper. Holes were drilled in the horizontal portion as follows: 1 central hole: #54 drill—center; 5 holes about central hole: #54 drill—1st circle; 10 holes about central hole: #54 –2nd circle; 15 holes about central hole: #51—3rd circle. These holes were spaced at the distances from center indicated in the detail drawing, and the holes were equally spaced in each circle.

The element was also constructed without the elevated rim shown, with a serrated rim, and with rims of various heights. The outside shoulder shown on the element was intended to allow height extension by stacking plain copper rings. Our limited experiments showed that a certain vertical extension of rim increased sensitivity. Too high extension of the rim interfered with the flame, however, and sensitivity dropped. Copper gauze and copper bus bar spirals were much less satisfactory. The massive construction is desirable since there is considerable flaking-off of cupric oxide in use.

METHOD

The apparatus is connected as shown in the block diagram in Fig. 1. Under the operating conditions already mentioned 1–25 μl of the compound under investigation was injected into the Fractometer, using an Agla syringe. The following compounds were investigated: methyl chloroform, methylene chloride, carbon tetrachloride, chloroform, and ethylidene chloride. All of these materials are important industrially, and at the same time present more or less toxic hazard in use. The effluent gas from the column is directed by means of a number 20 gage 6-inch stainless steel hypodermic needle into the atomizer of the flame photometer.

It was found, after numerous experiments, that a peak was always registered on the second recorder whenever the peak on the chromatograph recorder represented a chlorinated hydrocarbon. Conversely, no peak appeared on the second recorder for nonchlorinated peaks.

RESULTS

For qualitative analysis it is a simple matter to start the instruments, inject sample and compare the two charts obtained. Using the second chart the vapor chromatogram is labeled with respect to chlorinated hydrocarbon peaks.

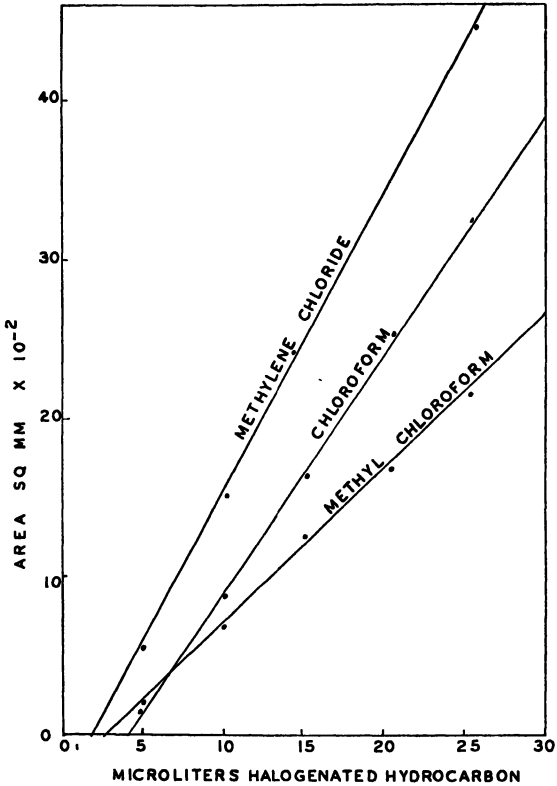

FIG 3 Peak areas versus microliters injected for three compounds.

Attempts were made to derive quantitative relationship from the peak areas on the second recorder chart. It was found that the compounds cited each gave a straight line for peak areas versus microliters injected (Fig. 3). It also appears that the lower the boiling point of the compound the steeper the slope for the same percentage of chlorine.

From the results obtained it seems impossible to identify a halogenated compound from its halogen content. Too many variables are involved. However, one can measure the amount of chlorine quantitatively when one is working with a known system.

CONCLUSIONS

The above procedure was worked out primarily to enable the busy analyst to pick out halogenated hydrocarbon peaks without any more attention than is necessary to inject the sample. We consider this completely justifies the procedure presented.

However, it became obvious in working with it that the quantitative aspects might well be explored with profit. At the same time we believe that improvement in Beilstein sensitivity might result from careful investigation of burner design, possible use of a hotter flame, and a more suitable filter, etc. We believe it would be interesting to use an element constructed of cupric oxide rather than copper or possibly to use a porous ceramic plate impregnated with cupric oxide. In the foregoing we have considered "halogenated" as synonymous with "chlorinated." In our work this is essentially true. As is well known, however, brominated and iodinated compounds would also give a positive response with the copper burner if present.

The method outlined is not presented as a fixed and final method, as already mentioned. It has demonstrated its practical usefulness in our laboratory, and it may be hoped that others may find it useful and possibly extend the scope of the method.

ACKNOWLEDGMENT

We wish to acknowledge the cooperation of Mr. G. Kronmueller of this laboratory who provided the inspiration for the automatic recording of Beilstein tests.

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CHAPTER XXX

New Approaches to the Resolution of Olefins

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Attempts to analyze low molecular weight paraffins and olefins by gas chromatography have received considerable attention during the past few years. Hydrocarbon mixtures which have proven particularly difficult to resolve are ones containing propane, propylene, *n*-butane, isobutane, butene-1, isobutylene, *cis*-butene-2, *trans*-butene-2, and butadiene. Several methods have been used in the analyses of these mixtures. Specific polar liquid substrates such as dimethylsulfolane (*6*), dimethylformamide, and acetonyl acetone (*7*) have yielded some favorable results at low temperatures. Indeed, the use of silver nitrate dissolved in organic solvents (*2*, *3*) has also proved useful in such separations by forming unstable complexes with olefins. Janak (*8*) has resolved paraffin-olefin mixtures by a subtractive technique using molten maleic anhydride to react with the butadiene present. More recently, Barnard and Hughes (*1*) have used a technique of physically mixing two packings in one column. While each of these methods is quite satisfactory for resolving some of the C_3–C_4 paraffins and olefins, the resolution of all nine of the hydrocarbons described above is quite difficult. Long columns and temperatures below ambient are generally required.

Recently Eggertsen and his co-workers (*4*, *5*) studied the separation of C_5–C_7 saturated with liquid modified columns consisting of 1.5% squalane on Pelletex (furnace black) Considerable information was obtained with such columns because their naphthene-paraffin selectivities are in reverse order compared with liquid-type columns.

The present approach to the problem of resolving C_3–C_4 paraffins and olefins involves the use of specially prepared liquid modified adsorbents. Two commercially available adsorbents, Florisil and Florex, were treated with aqua regia prior to their use in gas chromatographic columns. Various liquids were used to modify the adsorbent in this study. These ranged from nonpolar tetradecane to the highly polar β,β'-oxydipropionitrile. Particular emphasis was directed toward the effect of the amount of liquid phase on the solid adsorbent. Conditions were then found for preparing a column

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which would effect the resolution of the paraffin-olefin mixture in relatively short emergence times.

EXPERIMENTAL

Aqua Regia-Treated Adsorbent (12)

To 500 g adsorbent in a 3 liter beaker was added 1700 ml aqua regia. This mixture was gently boiled for one hour, then diluted with water and decanted. Washing was continued until the solution was almost neutral; 10 ml of 10% ammonium hydroxide was added and the water-washing was continued until the solution became neutralized. The adsorbent was washed on an 80-mesh screen to remove the fines and then dried in an oven at 130° C overnight (60–80 mesh material was used for preparing all columns). When these adsorbents were used without prior aqua regia treatment, little or no resolution of the hydrocarbons occurred.

Adsorbents

Florisil (Floridin Co.), a synthetic magnesia-silica gel catalyst and adsorbent and Florex (Floridin Co.), a naturally occurring fuller's earth which has been calcined, were the adsorbents used.

Supported Liquids

Tetradecane (Matheson, Coleman and Bell), dimethylsulfolane (Matheson, Coleman and Bell), Tri-*m*-tolyl phosphate (Distillation Products Industries), and β,β'-oxydipropionitrile (Distillation Products Industries) were the liquid modifiers.

APPARATUS

A Perkin-Elmer Model 154B equipped with a gas sampling valve was used in this study. All columns were made of ¼-inch OD copper tubing and were loaded in the conventional way with vibrating. The carrier gas was helium which was operated at 15 psi for the 10-ft columns and 30 psi for the 20-ft columns. This gave flow rates of 65 ml/min. All chromatograms were made at 25° C.

RESULTS AND DISCUSSION

Separations of the olefin-paraffin mixture were studied using dimethylsulfolane, β,β'-oxydipropionitrile, tri-*m*-tolyl phosphate, and tetradecane as the liquid modifiers. Florisil was used as the adsorbent although Florex is comparable in action. The percentage of supported liquid was varied from 1–5% and the effect on resolution factors studied. Concentrations

TABLE I

Resolution Factors for Butene-1 and Isobutylene Using Liquid Modified Adsorbents

	Dimethylsulfolane				β,β'-Oxydipropionitrile			
	1%	2%	3%	5%	1%	2%	3%	5%
S	0.17	0.19	0.10	0.05	0.12	0.10	0.10	0.06
Q	14.30	14.60	14.60	14.60	16.00	18.00	15.30	15.80
R	2.43	2.87	1.46	0.73	1.92	1.80	1.53	0.95
	Tri-*m*-tolyl phosphate				Tetradecane			
	1%	2%	3%	5%	1%	2%	3%	5%
S	0.10	0.10	0.07	0.05	0.15	0.14	0.13	0.12
Q	15.80	16.50	16.00	15.00	7.8	12.30	12.00	15.40
R	1.58	1.65	1.12	0.75	1.17	1.72	1.56	1.85

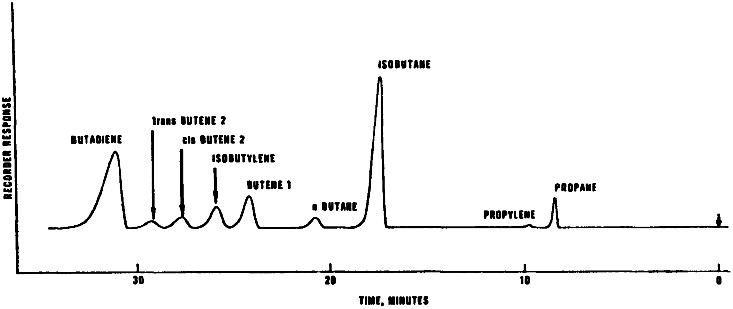

Fig 1 Chromatogram of hydrocarbons using a 20-ft column containing dimethylsulfolane on aqua regia-treated Florisil.

in excess of 5 % produced a liquid partition column with diminished resolution.

Relative peak separation, relative peak sharpness, and resolution values were determined according to the method of Jones and Kieselbach (9).

$$S_{12} = \frac{t_2 - t_1}{t_1}$$

$$Q = \frac{t_x}{w}$$

$$R = QS_{12}$$

where S_{12} = relative peak separation of butene-1 and isobutylene; Q = relative peak sharpness of butene-1; R = resolution of butene-1 and isobutylene; t_1 = elution time of butene-1; t_2 = elution time of isobutylene; t_x = elution time of butene-1; and w = width of peak as measured at the base-line intercepts of the tangents to the peak.

Table I shows the separation factors obtained using the different supporting liquids and varying their percentages. The high Q values indicate an efficiency of over 400 plates per foot of column measured on the butene-1 peaks. Selection of the 5% dimethylsulfolane column as the most useful is based on the over-all resolution of the paraffin-olefin mixture. Whereas a 1 or 2% column resolves butene-1 and isobutylene to a greater extent, *cis*-butene-2 is eluted at the same time as butadiene. In general, as the liquid phase is increased from 1 to 5%, the resolution of butene-1 and isobutylene is decreased. At the same time, *trans*-butene-2 moves toward butadiene, thereby improving the resolution of the mixture

A chromatogram of a sample containing propane, propylene, isobutane, *n*-butane, butene-1, isobutylene, *cis*-butene-2, *trans*-butene-2, and butadiene is shown in Fig. 1. A 20-ft column of 60-80 mesh aqua regia-treated Florisil with a flow rate of 65 ml/min effected complete resolution in 33 minutes. When butadiene is not present in these mixtures, much shorter columns can be used.

Recent developments in the use of capillary columns with ionization detectors (*10*, *13*) offer another approach to the resolution of complex olefin-paraffin mixtures. Capillary columns of 100,000 plate efficiencies coated with nonspecific liquid phases can effect such separations. Considerably less efficient columns may be used with supporting liquids such as dimethylsulfolane.

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CHAPTER XXXI

Chromatographic Determination of Water in Hydrazine

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INTRODUCTION

The use of hydrazine requires an accurate and relatively rapid method for the determination of the amount of water in hydrazine. To meet this requirement, the method which is described below was developed. Generally, water has been determined by a difference technique: The hydrazine was titrated with potassium iodate to the iodine monochloride end point using the conventional solvent technique (*10*, *12*, *16*) or with an internal indicator (*15*). The amount of ammonia or other basic materials was determined by difference from a direct acid titration of the material and the iodate titration (*5*, *9*, *14*). The amount of nonvolatile residue was determined by direct evaporation of the sample and weighing of the subsequent residue. The amount of water was, therefore, the difference between the summed percentages and 100.

Cordes and Tait (*4*) reported a spectrophotometric method for the direct estimation of water in several hydrazines in the near infrared region. They reported an accuracy of ±0.3% at the 95% confidence level in the range of 0 2 to 7.0% water by weight. Because of the special handling techniques which are necessitated by the hygroscopic nature of hydrazine, and the special size of the sealed cells needed, it was deemed that a gas chromatographic method for determining water in hydrazine would be desirable.

Several authors (*4*, *11*, *17*) have reported the use of Carbowax 1500 as the stationary phase in columns used to separate polar compounds. A standard 2-m column containing 30% by weight Carbowax 1500 on C-22 firebrick was prepared and it was found that the resulting retention volumes were so great as to make the column impractical. However, it was found that an 18-inch column of this material operating at approximately 80° to 90° C gave a satisfactory separation of water and hydrazine which could be used as the basis for an analytical method for the determination of water in hydrazine.

EQUIPMENT

Two instruments were used in this work. The determination of the retention volumes and the other chromatographic parameters were accomplished on a Consolidated Electrodynamics Corporation Chromatograph, Type 26-201, employing a filament type thermal conductivity cell and a standard Leeds and Northrup Speedomax, Model G 10-mv recorder. The flowmeter which was used to measure the helium flow was a Predictability Flowmeter, Model G-143 B, with sapphire ball, manufactured by the Manostat Corporation. The column temperature was monitored with a copper-constantan thermocouple employing a Leeds and Northrup Model 8662 Millivolt Indicator corrected for junction potentials. All quantitative analytical determinations were carried out on a Perkin-Elmer 154-C Vapor Chromatograph that was modified by the use of a Leeds and Northrup Model G Speedomax "Azar" Recorder, which has an adjustable millivolt range of 1 to 20 mv and a 1-second response over the full-scale. The recorder was set on a 5 mv span and the instrument was run at a sensitivity of 2 for water, 32 for hydrazine. All area measurements were carried out with a Model 4236 Planimeter manufactured by Keuffel and Esser Co. Two to 5 μl samples were introduced into both instruments by means of 50 μl syringes manufactured by the Hamilton Company.

PREPARATION OF COLUMNS

The chromatographic columns were made of aluminum tubing ¼ inch OD and 18 inches long. They were packed with Johns-Manville C-22 firebrick which had been crushed and sieved to 30–60 mesh and had been coated with Carbowax 1500 according to the method of Eggertsen *et al.* (*7*). Thirty grams of Carbowax 1500 was dissolved in sufficient absolute methanol to insure complete solution. This solution was then added to a beaker containing 100 g of the C-22 firebrick and the slurry stirred for ½ hour. The methanol was removed completely by evaporation at 110° C for 4 hours. The columns were packed by sifting the coated firebrick into one end of the column with the aid of a vibrator and the ends plugged with Pyrex glass wool. The ends of the columns were prepared and the columns shaped as required by the instrument in which they were being used. The columns were inserted in the instrument and stabilized by flushing with helium at operating temperature for 2 hours.

MATERIALS

Commercial hydrazine obtained from Olin-Mathison was used for the determination of retention volumes. Standard hydrazine was prepared by ammonolysis in this laboratory from hydrazine sulfate (Matheson, Coleman, and Bell, Reagent Crystal) (*2*, *3*, *8*, *13*). The unsymmetrical dimethylhydrazine which was also used in the determination of retention volumes was commercial grade material and was obtained from the Westvaco Chlor-Alkali Division of the Food Machinery and Chemical Corporation.

EXPERIMENTAL

The retention volumes of hydrazine, water, and unsymmetrical dimethylhydrazine were determined at temperatures of 81.5°, 85.8°, 89.9°, and 91.8° C and a flow rate of approximately 130 ml of helium/min calculated at 1 atmosphere and 70° F. The flow rate was accurately measured and the data reduced as recommended by Ambrose, Keulemans, and Purnell (*1*). The corrected retention volumes, corrected for total gas volume ($V_R^0 - V_G^0$), are given in Table I. A plot of these values vs $1/T$ is shown in Fig. 1. A sample chromatogram is shown in Fig. 2. This illustrates the available separation obtained with this column. It should be noted that the peaks are not symmetrical. The retention time on each peak was measured from the maximum as shown. Slight deviations in the maxima occur, especially in hydrazine, with a variation in sample size. Accordingly the

TABLE I

CORRECTED RETENTION VOLUME ($V^0_R - V^0_G$)

					Average
Test No. A. $T_c = 81\ 5\ C\ \frac{1}{T} = 2.82 \times 10^{-3}$					
UDMH	439	426	418	432	429
H_2O	1042	1042	1065	1076	1056
N_2H_4	3202	3139	3142	3158	3160
Test No. B. $T_c = 91\ 8\ C\ \frac{1}{T} = 2\ 74 \times 10^{-3}$					
UDMH	292	273	288	297	288
H_2O	690	641	627	672	658
N_2H_4	1951	1890	2090	2068	2000
Test No. C. $T_c = 85\ 3\ C\ \frac{1}{T} = 2\ 79 \times 10^{-3}$					
UDMH	359	359	361	359	360
H_2O	882	887	874	889	883
N_2H_4	2588	2591	2581	2599	2590
Test No. D. $T_c = 89\ 9\ C\ \frac{1}{T} = 2.755 \times 10^{-3}$					
UDMH	303	305	306	310	306
H_2O	747	744	748	749	737
N_2H_4	2157	2232	2114	2169	2168

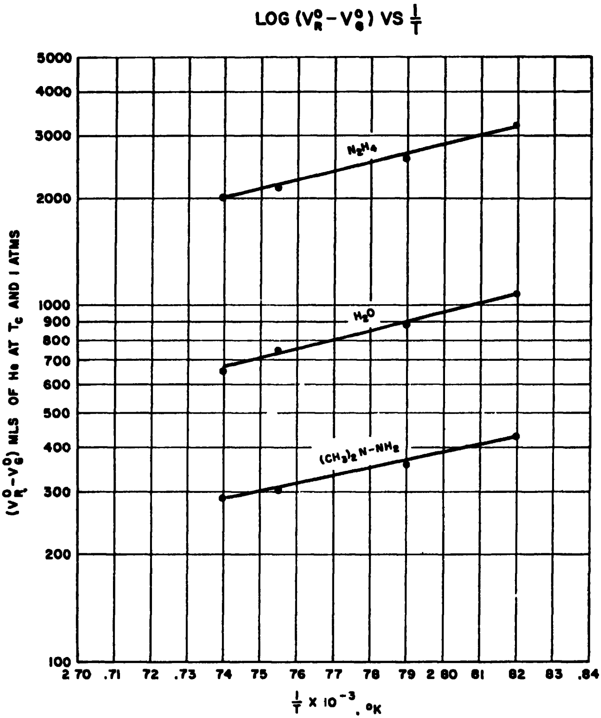

FIG. 1 Volume versus $1/T$.

sample size was maintained approximately constant (5 μl) and an average retention volume was used in each case. The chromatogram also shows a peak for ammonia, which was added to the mixture, since it might be present in the standard hydrazine solution prepared by ammonolysis. The retention volume was not calculated because the peak maximum was not constant. This was assumed to be caused by variations in sample size and speed of introduction which would tend to be magnified by the use of a short column. If an analysis for ammonia is desired, the column could be lengthened and the column temperature reduced which would result in a larger retention volume and a more stable peak maximum.

The area measurement technique was employed in the quantitative analysis of water in hydrazine to eliminate the effect of variation in sample size. The column temperature was 80° C and the flow rate comparable to

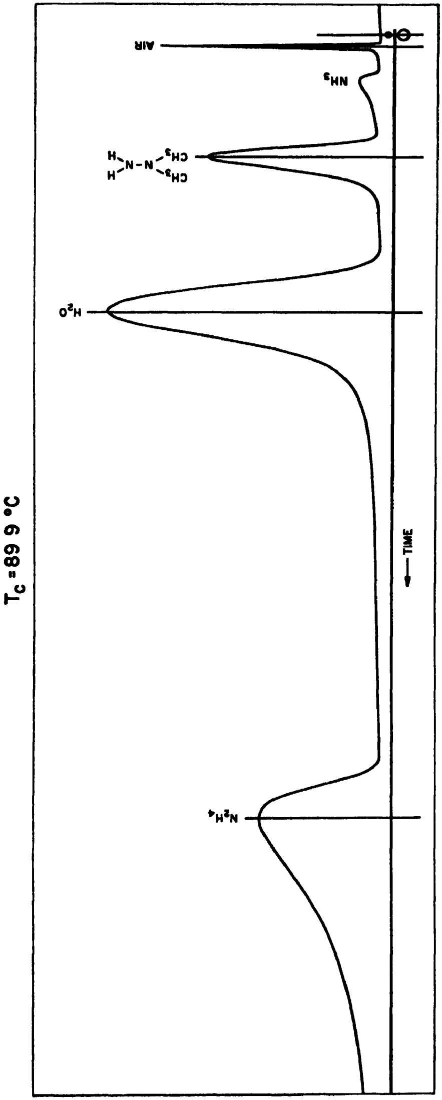

FIG. 2. Sample chromatogram

that used in the determination of the retention volumes. A chromatogram of the standard hydrazine was obtained and the material was found to contain water. Additional water was quantitatively added to the standard hydrazine and the resultant solution was analyzed chromatographically. The change in percentage of the total area was related to the weight per cent of water which was added and the percentage of the water in the standard solution was calculated. Additional water was then quantitatively added and the resultant solution was again analyzed. A plot of the percentage of the total area which corresponds to the water peak versus the calculated weight per cent water in the sample was made. This plot is shown in Fig. 3. Two values for water in the standard samples used are also included in this figure. As is seen, a linear relation exists and the slope of the line passes through the origin of the graph. The accuracy of the method is estimated to be ±0.05-0.09% absolute.

The precision of the analysis was determined by carrying out several runs on the same sample. Table II gives the results of two such analyses.

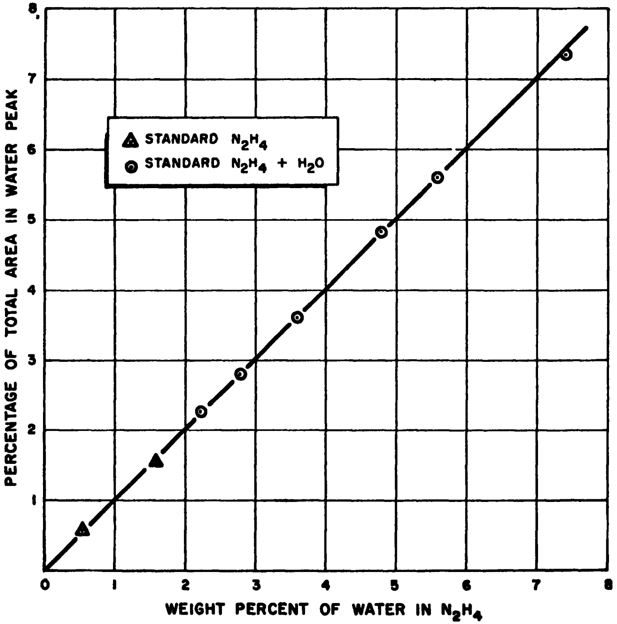

Fig. 3. Percentage total area under water peak versus weight per cent water.

TABLE II

RESULTS OF SEVERAL RUNS OF SAME SAMPLE

Sample A Test no.	Wt % H_2O
1	1.52
2	1.57
3	1.61
4	1.54
5	1.60
6	1.61
7	1.50

Mean: 1.56%.
Average deviation of a single determination: ±0.05%.

Sample B Test no.	Wt % H_2O
1	0.62
2	0.59
6	0.54
4	0.49
5	0.51
6	0.56
7	0.55

Mean: 0.55%.
Average deviation of a single determination. ±0.05%

DISCUSSION AND CONCLUSION

From the above presentation, it is obvious that an accurate and relatively rapid determination of water in hydrazine can be carried out gas chromatographically by using a short Carbowax 1500 column. The area measurement techniques gave linear results within the range of water concentration of interest. However, the separation is such that a greater amount of water could readily be determined with proper calibration. This column also may be used to determine water in unsymmetrical dimethylhydrazine. By proper adjustment of column length and temperature, the ammonia could also be determined.

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CHAPTER XXXII

Determination of Dissolved Oxygen in Petroleum Liquids

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INTRODUCTION

A need for a rapid and precise method for determining dissolved oxygen often arises in the petroleum industry. Because air surrounds all processing units, transfer lines, and storage tanks, oxygen is hard to keep out of process streams. Even small amounts of dissolved oxygen can markedly affect the efficiency of refinery processes, and accumulation can lead to explosion hazards. In controlling some operations, it is desirable to be able to distinguish between 0.2 and 0.4 ppm of dissolved oxygen, on a routine basis.

Analytical methods that have been proposed for measuring dissolved oxygen in hydrocarbons (*1*, *2*, *4*) lack adequate detectability. A gas-chromatographic method proposed for analyzing products of combustion makes use of a molecular sieve for the determination of oxygen in gases (*3*). Such an approach should be useful for petroleum liquids if the oxygen in a large sample could be quantitatively and conveniently recovered for measurement.

A method has been developed that handles samples 500 to 1000 times larger than are customary in gas chromatography. Samples are introduced from bombs that are attached to and become an integral part of the chromatographic apparatus. A molecular sieve preceded by a liquid partition agent and a solid adsorbent separates the oxygen from the hydrocarbons and other dissolved gases. The required detection is achieved conveniently with conventional rugged and dependable instrumentation.

APPARATUS

A flow diagram of the apparatus is shown in Fig. 1. Helium carrier gas is supplied at a constant pressure to an 8-liter surge drum. Three lines from the surge drum, each equipped with a needle valve to provide the desired flow, serve three distinct functions.

One line transports carrier gas to the sample-introduction point and thence to the chromatographic partition column and detector. A differential-pressure flow controller* maintains a constant pressure drop across the needle valve despite any pressure surge during sample charging. A

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* The Moore Differential Pressure Controller Model 63SU is satisfactory.

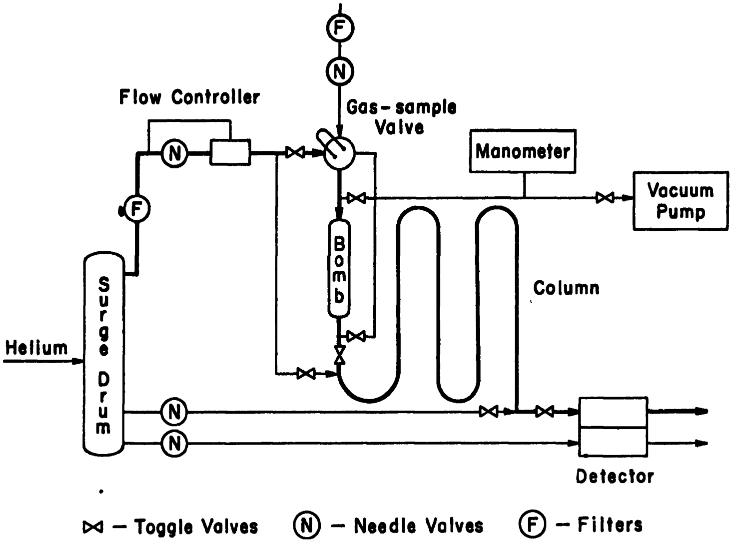

Fig. 1 Apparatus for determination of trace oxygen

gas-sample valve with a 0.25-ml sample-measuring loop is used to introduce air for calibration. Metallic micropore filters protect the gas-sample valve and the flow controller from abrasives.

A second line transports helium to the reference side of the detector; the third provides helium for regenerating the column by back-elution after the determination is complete.

The chromatographic partition column consists of: (1) A section 14 ft long and $\frac{3}{8}$ inch in diameter containing 30–60 mesh firebrick coated with silicone oil in a ratio of 55 gm of firebrick to 45 gm of silicone oil. (2) A section 3 ft long and $\frac{3}{8}$ inch in diameter containing 30–60 mesh activated cocoanut charcoal. (3) A section 6 ft long and $\frac{1}{4}$ inch in diameter containing 10–60 mesh 13 A molecular sieve. The three sections are packed individually and then soldered together to form a single gas-tight unit. Liquid and gaseous hydrocarbons are retarded on the silicone and charcoal sections; oxygen and other fixed gases pass through to be separated from each other by the molecular sieve. Heating is provided so that the hydrocarbons can be vaporized and back-eluted readily during regeneration.

As the detector, any commercially available thermal conductivity cell will serve. A recorder with 1 mv full-scale sensitivity is required.

Sample bombs, especially designed to hold high vapor pressure hydrocarbon liquids, are made by attaching a stainless-steel valve to each end of a stainless-steel ⅛-inch pipe nipple 6 inches long. The possibility of air infiltration is minimized by orienting the valves so that the tails of the arrows on the valve bodies face toward the bomb. Each bomb holds about 5 ml of liquid.

PROCEDURE

A flow of 150 ml/min of helium is established through the column and measuring side of the detector, and of 5 ml/min through the reference side. A filled bomb is attached with compression-type tube fittings, and the air is evacuated from around the fittings. By operating the appropriate valves, carrier gas is routed to the top of the bomb, and the contents are swept into the chromatographic column. Sudden changes in pressure may cause the base line on the recorder chart to be temporarily upset, particularly if the sample has a high vapor pressure. The flow controller quickly compensates for the pressure surge, and the base line recovers in a few seconds.

Oxygen, separated from all components except argon, is eluted in about 4 minutes. The argon content is too low to contribute a significant error to the determination. Oxygen is recorded as a curve relating millivolts of detector output to time.

After the oxygen peak has been recorded, the bomb is removed and flow through the column is reversed Hydrocarbons are vented at the point where the bomb was connected. The column is then heated to about 300° F and held at this temperature for 10 to 15 minutes until no more hydrocarbon is removed. Back-elution is continued for about 15 minutes, or until the column has cooled to room temperature. About 300 samples have been run through a single column without loss of efficiency.

Calibration data are obtained by passing precisely known volumes of air through the chromatographic columns and measuring the area under the oxygen peak. The oxygen content of the sample is calculated by comparing the area under the curve with areas obtained by analyzing known amounts of air, introduced with the gas-sample valve. The true volume of the sample-measuring loop and the volume held up in the valve ports must be measured to permit precise estimation of the air added. Smaller quantities can be introduced by reducing the pressure in the sample-measuring loop.

DISCUSSION

Replicate analyses of three hydrocarbons "off the shelf" were made to show the precision of the method:

Analyses	Oxygen Range, ppm by weight	Avg. % Dev.
4	38–41	2.5
6	54–56	1.1
8	96–100	1.0

A precision of 1 to 3% is indicated at the range of concentrations one might expect to find in stored hydrocarbons.

In routine use on refinery streams, such precision is not achieved. Usually samples must be taken hot and under high pressure, and they frequently contain light hydrocarbon gases and hydrogen. Partial vaporization with preferential loss of oxygen is difficult to avoid. Consequently, duplicate determinations are recommended. Typical results for refinery streams are shown in Table I. Duplicates usually agree closely. When they do not, sampling is suspected and a fresh pair of samples is analyzed.

Accuracy of the method has been checked in two ways: determining oxygen added to a naphtha of previously determined oxygen content, and analyzing duplicate samples by the chromatographic method and by an independent method.

In the first tests, measured volumes of air were added in the column to naphthas containing 0.1 to 0.3 ppm of oxygen. Results for nine samples showed:

Added	0.3	0.5	0.6	1.0	1.0	1.9	1.9	18	19
Found.	0.2	0.5	0.5	0.9	0.9	2.2	1.8	16	18

Added oxygen below 1 ppm was recovered within 0.1 ppm; added oxygen to 20 ppm was recovered within 2 ppm.

Duplicate samples were analyzed by the chromatographic method and by a method based on the paramagnetism of the oxygen molecule. Dissolved oxygen was determined by stripping from solution with a stream

TABLE I

TYPICAL DUPLICATE ANALYSES OF REFINERY STREAMS

Oxygen, ppm			
0.1, 0.1	0.3, 0.3	1.6, 3.8	4.4, 4.7
0.1, 0.1	0.3, 0.3	2.6, 2.7	4.7, 4.8
0.1, 0.1	0.3, 0.5	2.6, 2.7	7.0, 7.4
0.1, 0.1	0.4, 0.4	3.3, 3.3	32, 32
0.2, 0.2	1.2, 3.4	3.3, 6.2	31, 34
0.2, 0.5	1.5, 1.5	3.9, 3.9	67, 75

of nitrogen and comparing the paramagnetism of the mixed nitrogen and oxygen with that of known mixtures (*5*). Three pairs of such tests showed:

Gas-chromatographic method	4 8	33	73
Paramagnetic method	2 9	33	70

In all cases, good agreement was obtained. With the stripping step, the paramagnetic method is not sensitive enough to determine oxygen in concentrations below 2 ppm.

Extension of the chromatographic method to the determination of oxygen in liquid butane and propane is being investigated. Other determinations for which the apparatus should be useful include the measurement of nitrogen, carbon monoxide, and methane in liquid hydrocarbons. All these constituents plus oxygen could be measured in gases by introducing the sample with the gas-sample valve.

SUMMARY

Dissolved oxygen in petroleum is undesirable because it creates refining problems and represents a potential explosion hazard. Gas chromatography permits the rapid and precise determination of 0.1 to 100 ppm of oxygen in petroleum fractions. By introducing 500 to 1000 times as much sample as is customary in gas chromatography, enough oxygen is admitted so that rugged and dependable instrumentation can be used. The chromatographic partition column is made up of three sections connected in series. The first section contains firebrick coated with silicone oil; the second, charcoal. Liquid and gaseous hydrocarbons are retarded on the first two sections. Oxygen and other fixed gases pass through to be separated from each other in the third section, which contains molecular sieve. Oxygen content is computed from the area under a curve relating thermal conductivity to time.

ACKNOWLEDGMENT

The author is indebted to J A. Perry, who initiated the development of the method and helped in the early phases of the work

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CHAPTER XXXIII

Ortho-Para-Hydrogen Analysis by Gas Chromatography

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INTRODUCTION

In the course of work on evaluation of ortho-para-hydrogen conversion catalysts it became necessary to analyze various mixtures of hydrogen isomers ranging from normal hydrogen to 100% para-hydrogen. Gaseous molecular hydrogen at ambient temperature is normally composed of a mixture of 25% para-hydrogen and 75% ortho-hydrogen (*1*). A para-hydrogen molecule is one in which the two hydrogen nuclei have opposite spins. An ortho-hydrogen molecule is one in which the hydrogen nuclei have the same spin.

These spin isomers have slightly different physical properties, such as boiling point, melting point, specific heat, thermal conductivity. The equilibrium concentration of para-hydrogen in a mixture is a function of temperature, ranging from 100% para at −253° C (normal boiling point of liquid hydrogen) to 25% para at −40° C or above (*2*). The conversion reaction of ortho to para is second order with respect to ortho-hydrogen concentration (*3*). The attainment of equilibrium can be hastened with catalysts.

The conversion of ortho- to para-hydrogen evolves heat, roughly equal to the heat of vaporization of liquid hydrogen. Thus it is necessary to convert normal liquid hydrogen to the para form before storage to prevent evaporation loss. If this conversion is not done before storage, about 60% of the liquid hydrogen will be evaporated by the heat of conversion, even in the absence of any heat leak through the container.

With pure hydrogen, the determination of ortho-para ratio can be done by thermal conductivity, since the para-isomer has a higher thermal conductivity than the ortho-isomer. The thermal conductivity method is continuous and can be made very sensitive for small changes of composition. Purcell, Draper, and Weitzel (*4*) have reported a thermal conductivity unit capable of detecting 0.05% differential para content. However, the presence of impurities in the sample hydrogen would indicate a reduced para content. If the concentration of impurities exceeded 1 or 2% the sample gas would have a lower thermal conductivity than the pure normal reference gas and would then reverse the polarity of the signal from the cell. For example, a mixture of 100% para-hydrogen containing 1.3% nitrogen would have a thermal conductivity almost the same as pure normal hydrogen and could not be analyzed by direct thermal conductivity.

To eliminate this problem, gas solid chromatography was tried. Moore and Ward (*6*) have reported separation of these isomers by gas solid chromatography using alumina packed columns at 77° K with helium carrier gas. However, under these conditions all other impurities except neon would not be detected. From previous work in our laboratory it was known that helium, neon, hydrogen, and air could be separated at ambient temperatures on a carbon column. This was used for the following work.

APPARATUS

A 15-ft long by ¼-inch OD copper tubing column was packed with Burrell high activity carbon. The column was dried at 240° C for 4 hours using an argon purge. The analyses were done at 40° C using purified normal hydrogen carrier gas at 80 ml/min. A filament-type thermal conductivity detector was used, with a 0–1 mv recorder.

EXPERIMENTAL

Several problems required investigation before the method could be used with confidence: (1) The catalytic back-conversion effect of the column packing; (2) the effect of column contamination by air, water, CO_2, etc.; (3) the effect of carrier gas impurities; (4) the effect of impurities in the sample; (5) long-term stability of calibration.

First a series of 10-cc samples of known para-hydrogen concentration were passed through the unit. These mixtures were made immediately before use because the composition of ortho-para-hydrogen mixtures gradually changes back to normal at ambient temperature. Pure normal hydrogen (25% para) was used as the zero point (carrier gas). Fifty per cent para-hydrogen was prepared by passing pure normal hydrogen through a catalyst trap in liquid nitrogen (−196° C). One hundred per cent para hydrogen was prepared by passing hydrogen through a catalyst trap immersed in liquid hydrogen (−253° C). A plot of the peak heights versus per cent of para concentration gave a straight line (see Fig. 1). This result would be predicted on the basis of work by Weitzel (*5*) which showed the thermal conductivity of ortho-para-hydrogen mixtures to be a linear function of the para concentration. (Fig. 2 shows several runs of 50% para-hydrogen.) These tests indicated either no back conversion in the column or proportional back conversion.

To determine the extent of back conversion by the column, it was removed from the chromatograph. Tubing and valves were arranged so that the sample gas could be passed directly through the cell continuously.

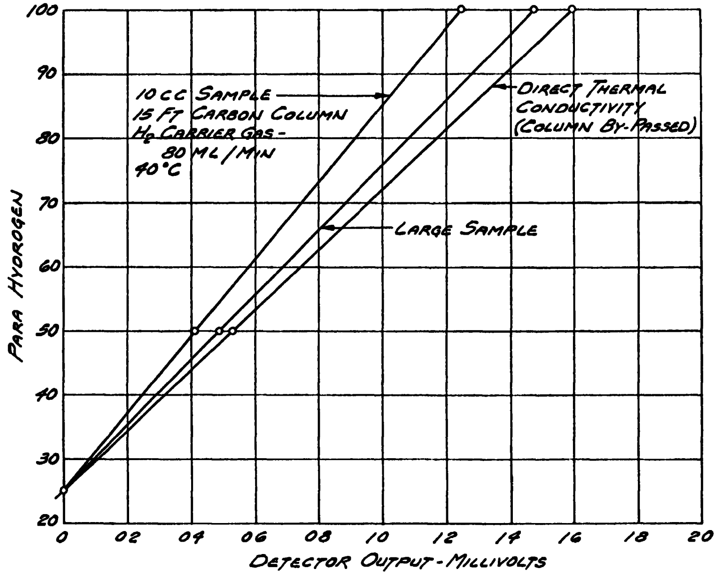

Fig 1 Plot of peak heights versus per cent of para concentration of three different samples

The three mixtures used previously were passed through the cell, one at a time, for about 5 minutes each. A plot of cell output versus per cent para gave a straight line as before, but at a different slope (see Fig. 1). This greater signal indicated back conversion in the column.

To determine the extent of this back conversion the column was returned and connections made to permit large samples to be introduced. About 30 ft of ¼-inch OD copper tubing was connected so that, after filling with sample, it could be placed in series with the carrier gas to the column. (No back conversion occurred in clean copper sample lines.) Mixtures of 50% para and 100% para were then passed through the column. These large samples resulted in flat topped peaks (see Fig. 3). However, a plot of maximum signal versus percentage of para again gave a straight line, but with a slope between the line for 10-cc samples, and the line obtained without the column (Fig. 1). This work showed that 8% of the para hydrogen in excess of 25% was back converted in the column. It was also concluded that the difference of signal obtained for 10 cc versus the very large samples was due to dilution of the sample hydrogen with carrier hydrogen while passing through the column.

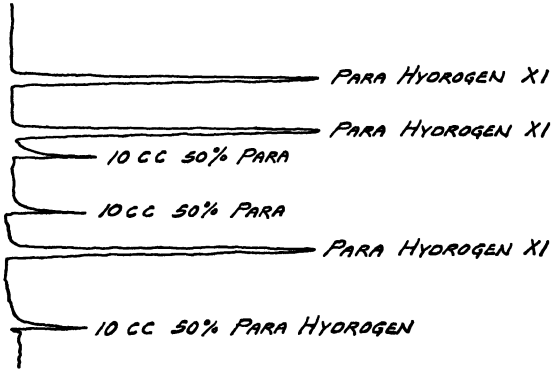

FIG. 2 Chromatogram of several runs of 50% p-hydrogen.

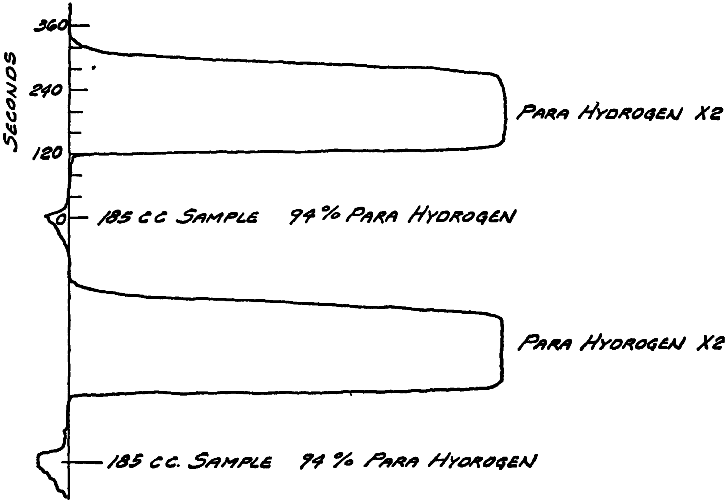

FIG 3. Chromatogram of large samples of p-hydrogen.

Oxygen is known to have a catalytic effect on ortho-para conversion. It might affect the analysis either by its presence in the sample or by accidental contamination of the column packing. To test this, several 10-cc samples of air were passed through the column, followed by several samples of 100% para-hydrogen. In all cases the peak heights obtained for the 100% para-hydrogen were the same as before the air contamination of the column. Apparently the oxygen was completely eluted from the column and did not cause any further back conversion.

The effect of nitrogen in the carrier gas was investigated only qualitatively. In all cases oxygen was removed from the carrier gas with a tube containing palladium catalyst. Several different unpurified hydrogen samples containing small amounts of N_2, Ar, and CH_4 were tried as carrier gas. No detectable change of calibration was found. However, at the times corresponding to the elution of nitrogen and argon small reverse polarity peaks were obtained (Fig. 4). This indicated less impurity in the sample hydrogen than in the carrier hydrogen. The lowest purity hydrogen carrier gas used probably did not contain more than 500 ppm total impurity.

As mentioned earlier, the peak height obtained for a given para-hydrogen concentration varied somewhat with sample size unless a very large sample was used. It is estimated that samples of 30 cc or larger would not show a variation of peak height with varying sample size, only longer or shorter flat tops.

By using a fixed 10-cc sample some reduction of peak height was obtained in the presence of impurities. However, during this work we were interested in the para concentration of pure hydrogen only. When impurities such as helium or air were found they indicated sample contamination. However a small amount of impurity, which would reduce the thermal conductivity of the mixture and prevent analysis by direct thermal conductivity, only reduced the quantity of hydrogen in the sample a small

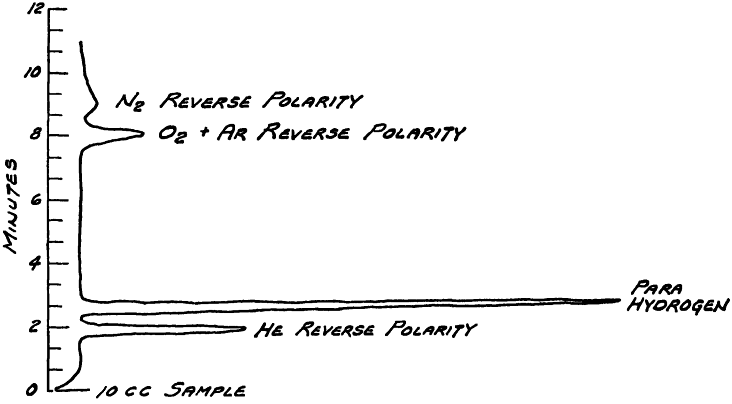

FIG. 4. Chromatogram of an unpurified hydrogen sample resulting in small reverse polarity peaks.

amount, and thus reduced the peak height obtained for para-hydrogen only a small amount. In order to get complete freedom from effects due to impurities in the sample it would be necessary to make a calibration of peak height versus volume of 100% para-hydrogen. Then a quantitative analysis of the sample would be necessary to get volume of hydrogen contained. This volume of hydrogen could then be placed on the calibration chart of peak height versus volume of 100% para-hydrogen. The para concentration of this hydrogen could be calculated by use of the equation:

$$\% \text{ para-H}_2 = 25\% + \frac{\text{peak height of sample}}{\text{peak height of equal volume of } 100\% \text{ para}} \times 75\%.$$

The calibration was checked frequently during a period of several months. The calibration at 100% para-hydrogen did not vary more than ±½% The calibration changes at lower para concentrations were proportionately less.

SUMMARY

Gas-solid chromatography has been used to analyze mixtures of ortho-para-hydrogen and to determine simultaneously the presence or absence of certain impurities. If desired, the impurities can be determined quantitatively. The calibration and column characteristics were stable, and not affected by impurities normally found in hydrogen.

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CHAPTER XXXIV

Linear Programed Temperature Gas Chromatography

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INTRODUCTION

The concept of increasing the column temperature during a gas chromatographic analysis was first described by Griffiths, James, and Phillips in 1952 (*1*). The major advantage of this technique, i.e., sharp, nicely spaced peaks from samples with wide boiling point range, was clearly demonstrated. Subsequent workers used the concept in the separation of hydrocarbons (*2–10*) alcohols (*2*, *3*), fatty acids (*11*), methyl ketones (*12*), sulfur compounds (*13*), alkyl chlorides (*1*), and radioactive bromides (*14*).

A number of apparatuses have been described (*2*, *3*, *8*, *15*, see pp. 60–61 of *16*, *17*) which allow the column temperature to be increased during a run, without seriously changing the detector temperature. In early work columns were withdrawn from cold baths and allowed to warm spontaneously, or fixed voltage was applied to column heaters. Because of line voltage fluctuations and changes in ambient temperature, reproducibility of these operations was too poor for widespread analytical use (*9*, *10*).

In 1958, Dal Nogare and Bennett (*2*, *3*), Harrison *et al.* (*8*), and Murray (*17*) reported devices for controlling the rate of temperature increase of the column. These workers obtained linear, reproducible heating rates by driving upscale the set-point of a temperature controller which was actuated by a thermocouple (or resistance thermometer) on the column. This thermocouple feed-back to a controller eliminates the effects of line voltage fluctuation and room temperature changes. The lines in Fig. 1 show the response of a thermocouple inside a column while the temperature is being programed. The deviation from linearity of the heating rates is less than 0.5%, but more important, the nonlinearity is reproducible. Figure 2 shows the reproducibility of actual chromatograms run under programed temperature conditions.

This refinement of instrumentation closed the gap which now makes the programed temperature concept a most practical technique for qualitative and quantitative analyses.

PRINCIPLES

Figure 3 is a typical plot showing the relationship of retention volumes measured at constant temperature with temperature (see pp. 27–29 of *16*).

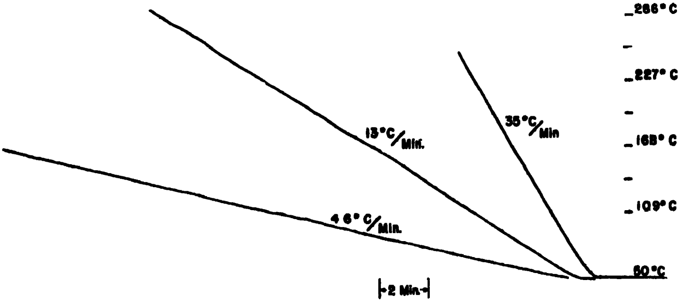

FIG. 1. Linearity of column heating rates.

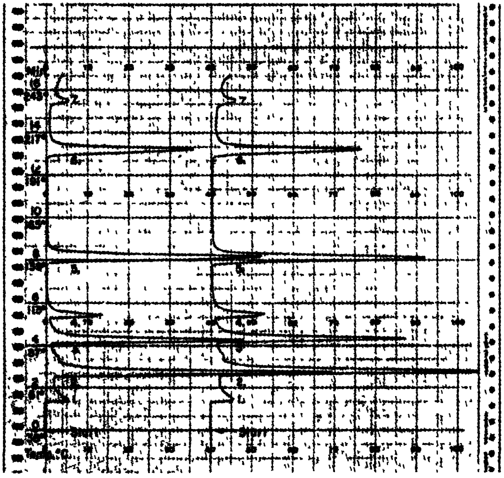

FIG. 2. Duplicate linear programed temperature chromatograms of an alcohol mixture. Key 1, methanol; 2, *n*-propanol; 3, *n*-butanol; 4, isopentanol, 5, cyclohexanol; 6, *n*-decanol; 7, *n*-dodecanol

From these data it is easy to calculate the average linear velocity at any temperature knowing the column length. The curved lines in Fig. 4 show the average linear velocity (v) plotted versus column temperature. If the temperature of the column is increased linearly during an analysis (from T_o to T_f) the abscissa can also be divided into time units (from t_o to t_f). If the area under one of the curves is accumulated until it equals the column length (time X velocity = distance), at this time and temperature the component will emerge from the column. The hatched portions in Fig. 4 show the respective areas for the homologs. From this plot it can be inferred that the relation between retention time and number of carbon atoms is nearly linear. Figure 5 shows experimental results to substantiate

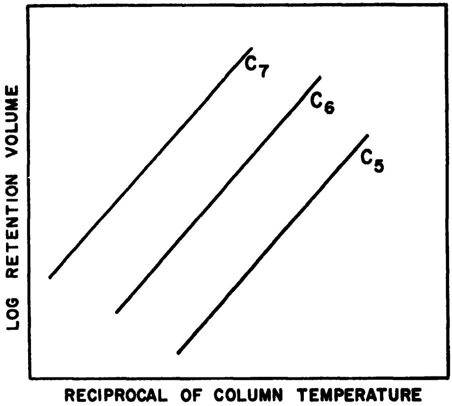

FIG 3. Typical relationship of retention volume and temperature for members of a homologous series

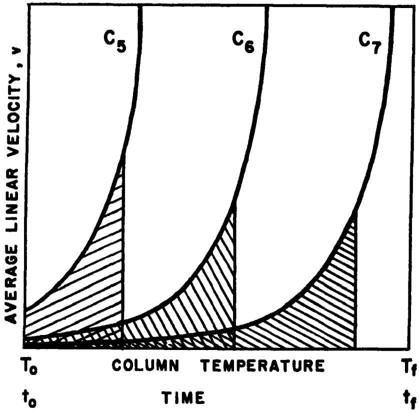

FIG. 4. Effect of temperature on average linear velocity of members of a homologous series.

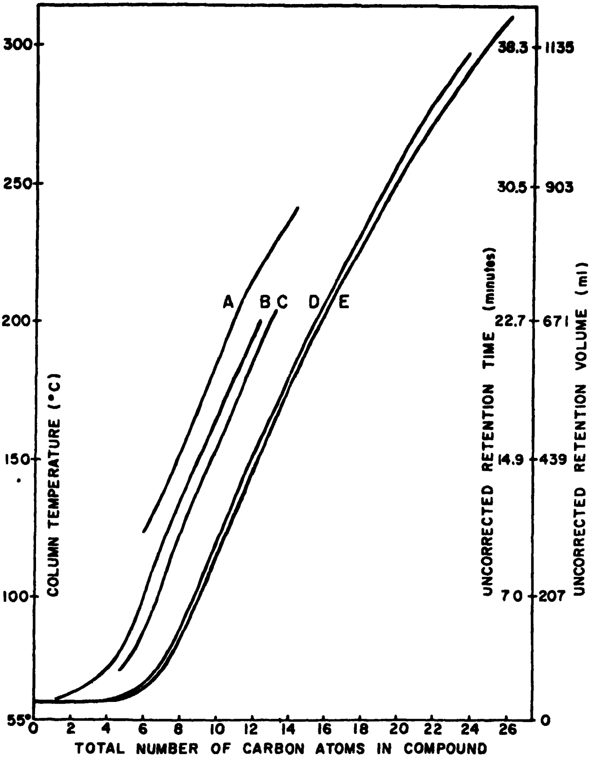

FIG. 5 Programed temperature retention data for members of five homologous series A dimethyl esters of normal dibasic acids, B. normal alcohols, C methyl esters of normal fatty acids, D: normal paraffins; E. 1-olefins of normal paraffins Column: 4-ft silicone gum on 30–80 mesh Chromosorb; helium flow rate 30 ml/min; starting temperature 55° C, linear heating rate: 6.4° C/min

the nearly linear relation. This is in contrast to the logarithmic relation for isothermal chromatography as inferred from Fig. 3.

The effect of linearly increasing the column temperature during the analysis is shown in a practical way by comparing the chromatograms of Figs. 2 and 6. In the isothermal run (Fig. 6) the early alcohol peaks were very sharp and were not completely resolved. In addition, component 6 showed a very low and broad peak, not very useful for analytical purposes, while component 7 did not appear as a peak within 76 minutes. The chro-

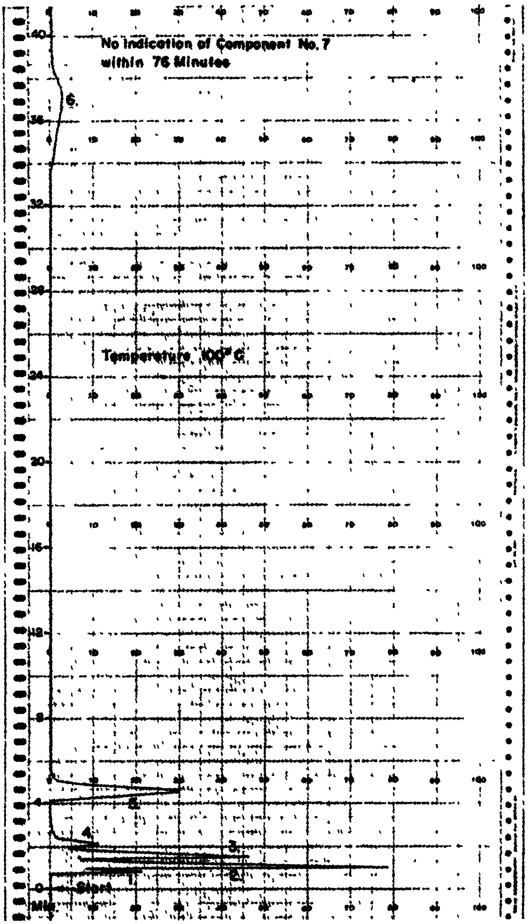

Fig. 6 Isothermal chromatogram of an alcohol mixture. Key 1, methanol, 2, *n*-propanol; 3, *n*-butanol; 4, isopentanol, 5, cyclohexanol; 6, *n*-decanol; 7, *n*-dodecanol Temperature 100° C, column 4-ft silicone oil (D-C 200)

matograms in Fig. 2 were run using the same sample, column, and flow rate. The temperature was 35° C at the start, and was linearly increased to 250° C. In these cases, all of the components emerged within 16 minutes as sharp and nicely resolved peaks.

RESOLUTION

It is difficult to compare the resolution of programed temperature technique with that of the isothermal method. The standard method of comparing column efficiencies by the number of theoretical plates cannot be applied to the programed temperature chromatograms (*18*). Resolution must be compared in two practical ways: (1) the ability to separate components of adjacent peaks, and (2) the ability to make accurate measurements on both of the resultant peaks.

Under specified conditions of column length and carrier gas flow rate, there exists a temperature at which optimum resolution of components A and B occurs. At higher temperatures the components are not as completely separated while at lower temperatures the peaks are more difficult to measure accurately. This temperature is not the same as that required for optimum resolution of B from C. Hence it is fair to say that the programed temperature technique offers nothing in the resolution of a *two*-component mixture but is of significant advantage in the resolution of mixtures containing three or more components. Using the isothermal technique with multicomponent mixtures, it is often necessary to compromise resolution for speed of analysis. This compromise is usually avoided with the programed temperature technique.

QUALITATIVE AND QUANTITATIVE INTERPRETATION

Under identical experimental conditions, programed temperature retention times (or retention volumes or temperatures) are as reproducible as with isothermal techniques (see Fig. 2). Figure 5 shows a plot of retention temperatures versus the number of carbon atoms for several homologous series. This plot is similar to that reported (see pp. 27–29 of *16*) for isothermal conditions where the *logarithm* of retention volume is plotted *versus* the number of carbon atoms. These presentations are of great value for the qualitative identification of unknown components.

The quantitative aspects of programed temperature gas chromatography are straightforward. Since the temperature of the detector and the carrier gas flow rate are maintained constant, the normal quantitative treatment is applicable.

Table I shows data of peak height and area for the separation of oxygen and nitrogen at various heating rates. The peak height increases as the heating rate is increased. The peak area is constant within our ability to inject 2 ml air samples via syringe (±3% relative). The oxygen content found is constant (±1%). It is our experience that the precision of results from programed temperature analyses is generally equal to isothermal analyses, and is significantly better in those cases where separation and

TABLE I

EFFECT OF HEATING RATE ON PEAK MEASUREMENTS[a]

Heating rate, °C/min	Oxygen peak		Nitrogen peak		Oxygen content[e]
	Height,[b] cm	Area counts[d]	Height,[b] cm	Area counts[d]	Per cent found
0	8.50	159	12.60	587	21.3
3.3	8.97	162	14.80	611	21.0
9	9.82	169	17.62	626	21.2
18	10.05	166	19.68	616	21.2
35	11.13	168	24.2[c]	617	21.5
		165 ± 4		611 ± 14	21.2 ± 0.2

[a] Two milliliters air separated on a 4-ft column of Molecular Sieve 5A. Starting temperature; 30° C; helium flow rate: 45 ml/min.

[b] Full scale = 50 mv

[c] Measured as 12.1 at 100 mv.

[d] Counts from Disc integrator, maximum count rate of 3000/min.

[e] Represents oxygen and argon.

peak shape are improved. Another advantage is realized from maintaining the detector temperature and carrier gas flow rate constant: the calibration of a component (by peak area) in one mixture is applicable to the analysis of the same component in another mixture even though the column, column temperature, or temperature program is different.

GENERAL AND SPECIFIC APPLICATIONS

The programed temperature technique offers real advantages as a scouting tool, particularly with samples of limited size. The first run indicates the boiling point range and complexity while giving qualitative and quantitative information. It is unnecessary to "hunt" for the proper temperature conditions. These same features make the instrument ideal for methods development work. Columns or column temperatures can be changed rapidly without affecting the detector temperature, thus eliminating the waiting period for the detector to reach thermal equilibrium.

The analysis of mixtures containing materials with widely different boiling points is the real triumph of the technique. Hydrocarbons or olefins from C_4 to C_{26} have been analyzed in a single run. In general, materials having boiling points between room temperature and 450° C can be eluted as sharp peaks in a single run (e.g., on a well-conditioned column of silicone gum).

The much-neglected gas-solid chromatography assumes new importance with the programed temperature technique. Figure 7 shows a chromatogram of fixed gases and low molecular weight hydrocarbons. This chromatogram is of real importance in that the gases of interest in respiration studies and many industrial processes, i.e., oxygen, nitrogen, carbon monoxide, and carbon dioxide, are separated on a single column. Similarly, all the saturated and unsaturated isomers of C_1 through C_5 hydrocarbons can be separated on alumina columns under programed temperature conditions.

The programed temperature technique is valuable for the analysis of trace levels of high-boiling impurities. These analyses are difficult to perform isothermally because of (1) tailing of the major component peaks and (2) the flat, broad shape of the impurity peak. However, if the column is maintained at a low temperature at the beginning of a run the major components can be completely eluted. Raising the temperature will then drive off the trace high boiler in a sharp easily measured peak.

This same concept has been applied to the analysis of very low level components. An ether extract containing only several parts per million each of three high boiling materials was to be analyzed. A 50 μl sample was injected while the column was held at a low temperature. The ether was eluted very rapidly but the high boilers remained on the early portion of the column. Four more 50 μl samples were injected in a similar manner so that the effective sample size was 0.25 ml. The column temperature was then raised and the three materials were eluted as three sharp, well-resolved peaks.

Large-scale separations for preparative purposes can utilize the advantages of the programed temperature technique (*19*) By the use of the proper temperature program the chromatogram essentially can be tailor-made. This avoids the very rapid manipulation of collection vessels. The ability to "clean up" a column of high-boiling residues by raising the temperature is an important feature in obtaining pure fractions. Figure 8 shows the separation of a 2 ml sample in a ¾-inch diameter column. The collected fractions were analyzed and showed less than 100 parts per million of the other components.

APPARATUS

All original chromatographic data presented in this paper were obtained on the F & M Scientific Corporation Model 202 Linear Programmed Temperature Gas Chromatograph. Figure 9 shows a picture of the commercial unit. This instrument is similar to that described by Dal Nogare and Bennett (*2*, *3*). Nine linear heating rates (from 3.3° to 48° C/min) are provided by driving upscale the set point of a 0° to 400° C temperature controller. The detector utilizes high-resistance thermistors (100,000 ohm at 25° C) to provide high sensitivity at elevated temperatures. The temperature of the detector is maintained constant from 150° to 300° C with a thermistor controller. A differential-type flow controller maintains the helium flow rate constant even though the pressure drop across the column changes when the column is heated. A moisture trap of Molecular Sieve 5A removes impurities from the helium which might otherwise collect on a cold column and be released as the temperature is raised.

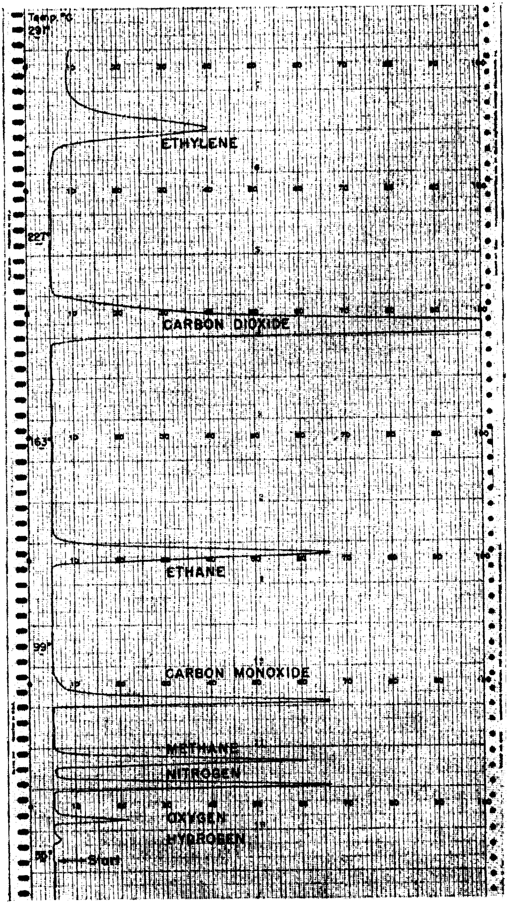

FIG. 7 Programed temperature gas chromatogram of a mixture of fixed gases.

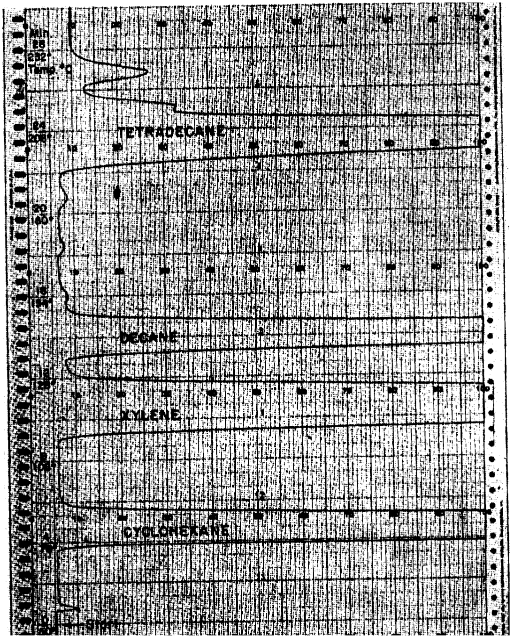

FIG 8 Gas chromatogram made during a large-scale separation.

SUMMARY

Programed temperature gas chromatography offers many advantages in the analysis of complex mixtures, such as, speed of analysis, resolution, qualitative and quantitative interpretation, determination of high-boiling trace components, and large scale separations. Popularity of the technique has been delayed by the lack of a device to provide reproducible heating rates, hence reproducible chromatograms. This lack has been overcome and the technique is finding wide application to diverse analytical problems involving components ranging from fixed gases to materials boiling up to 450° C.

A simplified explanation of the phenomenon occurring during a programed temperature analysis has been presented. This allows a graphical method of predicting retention time from isothermal data.

Resolution of the programed temperature technique is discussed along

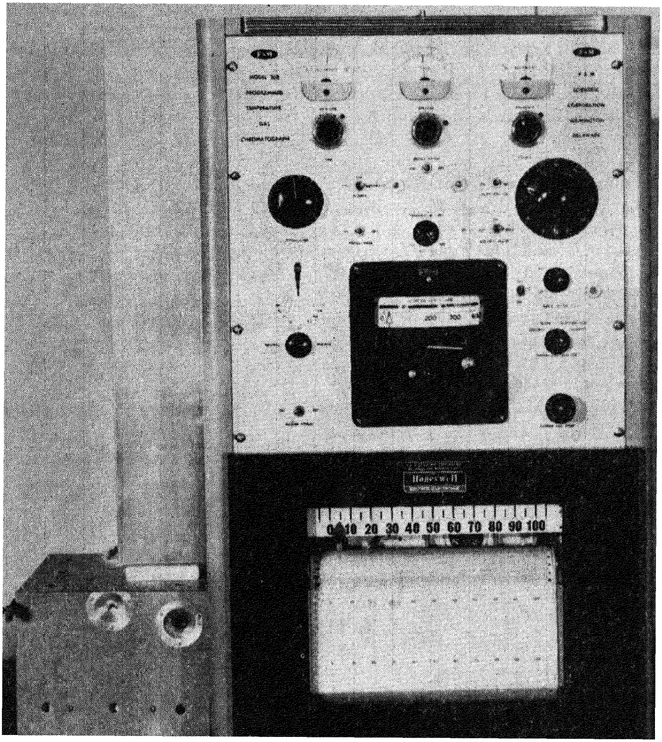

FIG. 9. The F & M Model 202 Linear Programed Temperature Gas Chromatograph.

with the qualitative and quantitative interpretation of chromatograms. Applications to gas-solid and gas-liquid chromatography are presented.

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Bibliography on Gas Chromatography. II

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The Proceedings of the First Gas Chromatography Symposium, held under the auspices of the Analysis Instrumentation Division of the Instrument Society of America, August 1957 included as a supplement a bibliography on gas chromatography We now continue this bibliography up to about June 1960

The first bibliography contained the publications up to the end of 1957. We included in this work some literature which was not available at that time. The numbering of references in this bibliography begins with 443, a continuation of the numbers given in the first bibliography.

The first bibliography predicted that "It might be anticipated . . that by the end of 1958, the number of articles which have appeared will have doubled the number referred to in this Bibliography " This prediction was quite true, as shown in the accompanying graph which indicates the increase in publications reviewed.

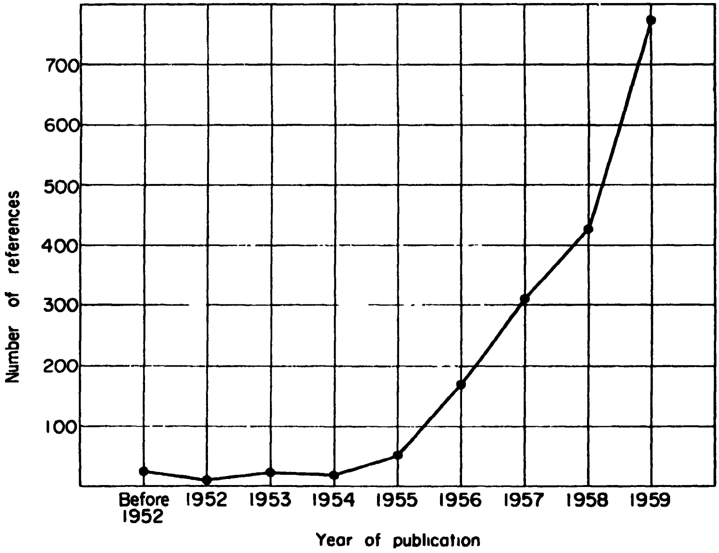

FIG. 1. The graph illustrates the increase in publications since the first volume appeared. Each point on the graph represents the number of publications in a given year that were included in the bibliographies of either one or both of the two volumes.

This graph shows that the literature about gas chromatography is beginning to be vast; this increase is particularly marked in the case of papers describing the use of gas chromatography as an analytical tool.

The increasing number of papers concerning applications of gas chromatography, presented at various meetings, make it quite impossible to survey this field in particular. In most cases the papers have not been published and, frequently, even the program of the meetings or the abstracts of papers are difficult to obtain. Two facts indicate this very well: the first bibliography listed only 41 papers presented at meetings which had not yet been preprinted or published; the number of such papers in this present bibliography is 235.

The general system of editing this bibliography is identical to that of the first bibliography, except that two deviations were made: (1) the language of the paper is always indicated if it is not English; (2) the *Chemical Abstracts* (*Chem. Abstr.*) quotations are only given for journals difficult to obtain in the United States.

The abstracts of the Gas Chromatography Abstracting Service (C. D. Lowry, Jr. and S. T. Preston, Jr., 80 East Jackson Boulevard, Chicago 4, Illinois) were of great help in compilation of the recent literature and will make the preparation of future bibliographies much easier. The author of this bibliography is also indebted to Dr. R. Kaiser who placed at his disposal the Proceedings of the two East German Gas Chromatography Symposia (1958 and 1959) which includes the text of 42 papers.

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